THE CONSTITUTION OF FURNACE SLAGS IN FERROUS PRACTICE.

THESIS FOR THE DEGREE OF PH.D.

presented by

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INTRODUCTORY.

During recent years great advances have been made in the study of the reactions taking place during the manufacture of steel by the two open hearth processes. With increased knowledge attention has come to be focussed less on the metal itself and more on the slag layer which forms on the surface of the metal bath. The important part played by this layer is now generally accepted and it is recognized that further advances in knowledge can only come with improved understanding of the complex materials composing it. The effect has been to concentrate attention on a new and fascinating branch of physical chemistry - the physical chemistry of the slag forming compounds at temperatures of 1200°C and over.

In this study much has been done, especially within the last few years, but much still remains to be done. The variables are so numerous, and the conditions so complex and difficult to reproduce in the laboratory that progress has necessarily been slow in many directions. Further the worker in this field finds himself, in many cases, bound by limitations imposed by nature, in that materials combining the properties of refractoriness, chemical inertness, strength, and impermeability to gases at high temperatures, necessary for the construction of his apparatus,do not exist.

In surveying the records of investigations a classification into two broad groups suggests itself. The first of these comprises investigations which concern themselves with the composition and constitution of slag and metal throughout the actual industrial process. The methods employed are chemical analysis and optical identification of mineralogical constituents to obtain data which on analysis, graphical or otherwise, will provide information concerning the fundamental reactions taking place. The second group is composed of researches into the properties of the known constituents of slags as such, or of simple combinations of these constituents, under laboratory conditions, in the hope that the data obtained may be of use

in elucidating the more complex relationships of the actual steel bath.

The two methods are, of course, complementary. The first gives information regarding actual furnace conditions; the second regarding properties of individual components. The drawback to the first, at least as far as the provision of fundamental physico-chemical data is concerned, is that the conditions are so complex that complete analysis of the data is difficult at the present stage. By the second method physical and chemical constants of the various materials involved can be obtained, and this has become increasingly important since the successful application in recent years of thermodynamical treatment to the reactions in the steel bath. Thermodynamics can always provide irrefutable information concerning the equilibria involved provided the required constants of the materials are known with sufficient accuracy. Unfortunately in many cases knowledge in this respect is very incomplete.

The present account treats of investigations which fall into the second group of the above classification, the materials investigated being important constituents of acid and basic slags. The data collected has been of two kinds; firstly, that concerned with the thermal equilibrium between phases, solid and liquid, information of considerable value from the point of view of a process in which the fusibility and solvent power of the slags are of prime importance; and secondly, that concerned with the chemical constants of certain of the materials and with the chemical equilibria dependent on them.

Somewhat arbitrarily a division into two parts has been made. Part I deals with important constituents of slags which are essentially acid in nature as occur in the acid open hearth process; Part II with constituents of basic slags such as are encountered in the basic open hearth process.

The arrangement adopted is as follows:

PART I : Investigations into the constitution of acid slags.

SECTION 1: The thermal equilibrium diagram of the binary system $MnO-SiO_2$.

SECTION 2: The thermal equilibrium diagram of the binary system FeO-MnO.

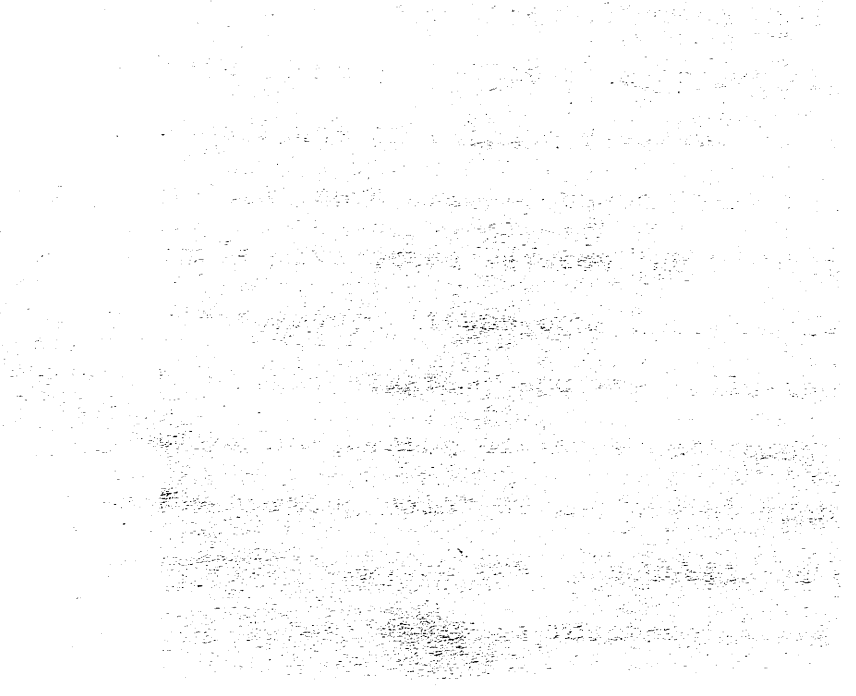
SECTION 3: The thermal equilibrium diagram of the binary system $FeO-SiO_2$.

SECTION 4: The constitution and properties of acid slags regarded on the basis of the ternary system $FeO-MnO-SiO_2$.

PART II : Researches on some of the constituents of basic open hearth slags with particular reference to the oxidising mechanism of such slags.

SECTION 1: The thermal equilibrium diagram of the binary system $CaO-Fe_2O_3$.

SECTION 2: Investigation of the dissociation of Fe_2O_3, monocalcium ferrite, and dicalcium ferrite.



PART I. Section 1.

THE THERMAL EQUILIBRIUM DIAGRAM OF THE BINARY SYSTEM $MnO-SiO_2$.

MnO and SiO_2, together with FeO, form the principal constituents of acid open hearth slags. (The three together make up between 80 and 90 per cent of the average acid slag.) A knowledge of the thermal equilibrium diagram of the system $MnO-SiO_2$ is therefore a matter of considerable importance.

An attempt to elucidate this diagram had previously been made by Doerinckel[1]. His results are based on cooling curves taken with melts in a platinum crucible, and are necessarily restricted to the more fusible compositions. Herty[2] has also investigated this diagram by observing optically the fusion and solidification of the necessary mixtures. This method involves considerable difficulties, particularly in the case of melts freezing over a range of temperature. Herty himself did not determine the high SiO_2 portion of the diagram, but took the generally accepted work of Greig[3] as being correct. Greig investigated the effect of various metallic oxides on the melting point of SiO_2 by a method which involved the quenching out of melts from different temperatures, and determining by optical examination the relative amounts of liquid and solid which had been in equilibrium at the moment of quenching. By this means it is possible to explore completely the liquidus and solidus lines of a phase diagram. In addition to the above Glaser[4] and Cain[5] have also proposed diagrams. There is, however, considerable divergence between the results of the various workers. For this reason, it was considered desirable to repeat the determination of this diagram, and the following is an account of the work. During the course of these determinations it was discovered that the melting point of MnO was at much higher temperature than previously supposed (see "Discussion of curves"), and hence it was considered advisable to redetermine the binary system MnO-FeO.

FIG. 1

MOLYBDENUM WOUND HEATING FURNACE.

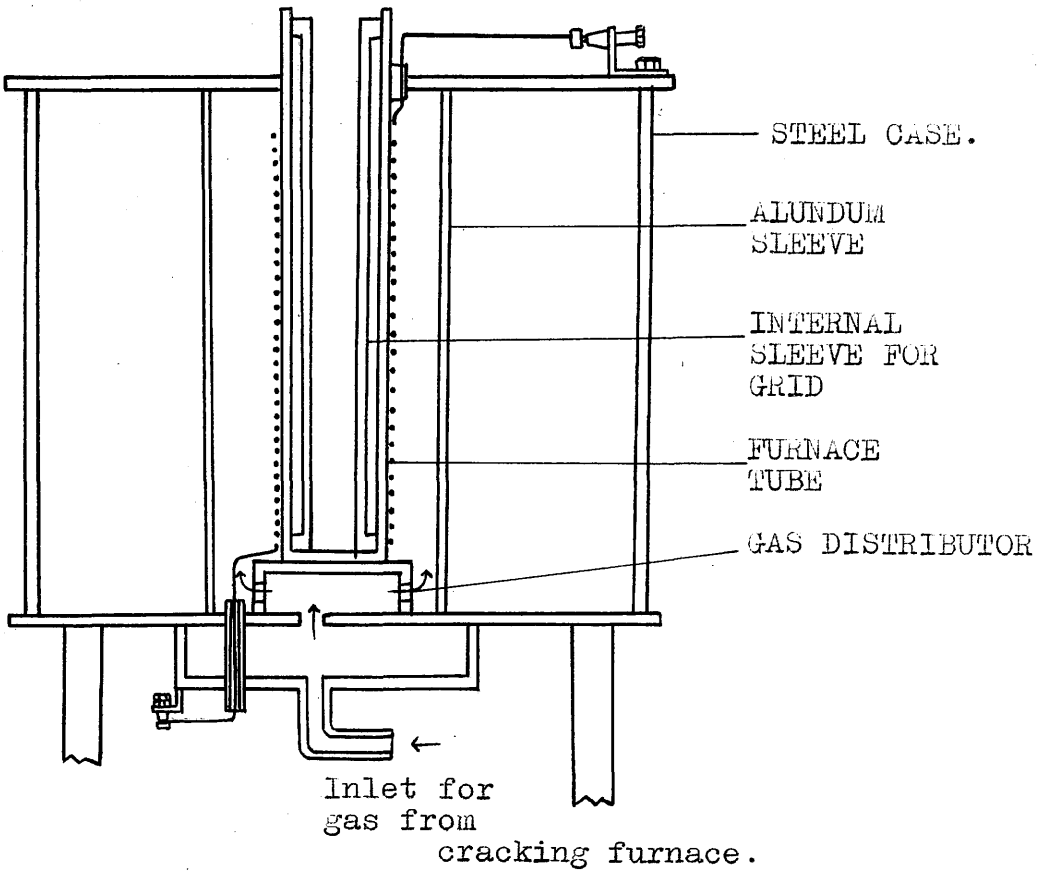
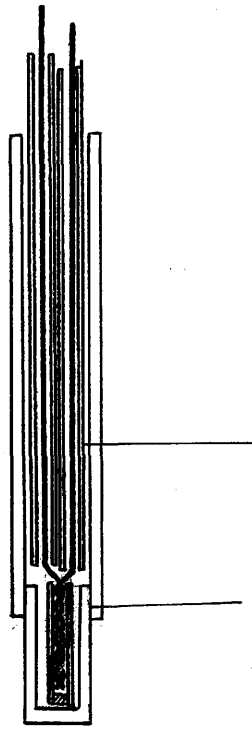


FIG. 2.



METHOD OF BUILDING UP THERMOCOUPLE SHEATH FROM CARBON RODS.

Details of Apparatus.

Furnace for melting. For the determination of thermal curves a vertical molybdenum-wound furnace, as described by Andrew, Maddocks, and Howat[6], was employed (see Fig 1). The heating element consisted of 41 feet of .04 inches diameter molybdenum wire wound on an alundum furnace tube, and carried a current of 30 amperes for a potential drop of 250 volts at a temperature of 1800°C. An internal alundum sleeve carried a grid of sheet molybdenum to protect the temperature-measuring thermocouple from the effect of the electric field of the winding at high temperatures. A mixture of hydrogen and nitrogen, got by cracking ammonia, passed to the furnace via the pipe in the bottom of the iron casing, maintaining a reducing atmosphere and preventing the windings from burning out.

As a result of experience, several alterations in detail were, however, carried out resulting in improved performance, and increased life of the windings. For example the diameter of the furnace tube was reduced to a minimum (2¾ inches internal diameter). The walls were made as thin as possible and the winding put on the tube with somewhat closer turns to concentrate the heat. In addition a very thick outer coating of alundum was put over the winding, which resulted in an increase in the rate of heating and in the maximum temperature attainable. The reason for this appears to be that transfer of heat to the melt takes place mainly by means of the gases introduced. These, to escape to the atmosphere, must pass from the outer airtight casing of the furnace through the porous alundum tube before emerging from the top, and thus they have their temperature raised by contact with the hot alundum which thus acts in the same fashion as checkers in regenerative practice. This has been verified in that attempts to construct vacuum furnaces have proved difficult, due, in part, to the absence of this means of heat transfer. A great thickness of alundum ~~of alundum~~ also acts as a protection against slagging due to the penetration of dust, and the life of the furnace is very much increased. It may be mentioned that

furnaces in use five days a week to temperatures in excess of 1600°C have been known to last as long as six months, when constructed on these lines, and a temperature of 1860°C has been recorded.

Experimental Procedure. At the commencement of work on this system the original technique employed by Andrew, Maddocks and Howat[6] was adhered to very closely. About 50 grams of the appropriate mixture was weighed out, and placed in a refractory crucible, while the point of a molybdenum-tungsten thermocouple, enclosed in a refractory sheath, was inserted in the mixture, and connected via a cold junction to a Tinsley potentiometer operating in conjunction with a mirror galvanometer and scale. Inverse rate heating and cooling curves were taken.

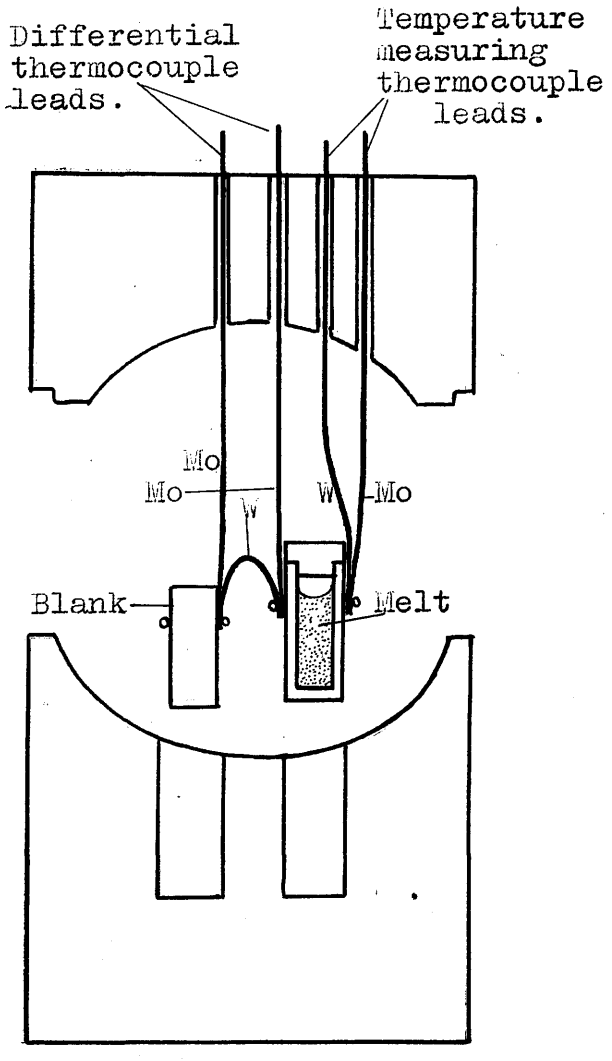
From the outset great difficulty was encountered. The choice of a suitable refractory was perhaps the chief of these, on account of the extremely reactive nature of the melts and the high temperatures involved. Of all the substances tried, "Salamander" proved the best but it invariably gave beads of metallic manganese due to reduction in all melts except those very poor in MnO. Further the only sheath of any use was one made of carbon, got by drilling out the centres of carbon arc electrodes, and these still further accentuated the reduction of MnO. Initially these sheaths also caused a great deal of trouble with the thermocouple due to uncertain readings, until it was found necessary to insulate both wires very completely from contact with the carbon. To achieve this both wires had to be covered with silica sheathing down as far as the join formed by twisting the two together, which was itself inserted in a seperate short piece, as indicated in Fig. 2. The result was, to avoid the use of too thick a sheath at the actual point, sheaths had to built up from two thicknesses of carbon rod, the point being sunk in a piece of smaller diameter drilled to a smaller bore (see Fig. 2). The thermocouple then behaved perfectly, but, even with these precautions, the amount of heat insulation taking place was considerable, and made the

detection of anything but large points rather uncertain. Even so, this method being the most promising tried up to that time, was employed until the true extent of the reduction with increasing MnO content was realised. Previous to this, however a considerable number of curves had been taken.

About this time it was noticed that the thermocouple wires, even when immersed directly in the melts, showed no sign of corrosion (though the readings became very erratic), and it was decided to try molybdenum itself as a refractory. Enquiries to the Tungsten Manufacturing Company elicited the fact that molybdenum crucibles could only be spun in America, and at a prohibitive cost. It was decided to drill out crucibles from the largest size of rod available, which was only 11 millimetres in diameter. These crucibles were about an inch in length and the size of the melt was limited to about two grams in each case. Molybdenum lids were fitted, and at first these were drilled to allow insulated thermocouple wires to pass through them, the points being inserted directly in the melt. Later to eliminate erratic readings, the point was bound to the outside of the crucible with molybdenum wire, on the assumption that, molybdenum being a good conductor of heat, the thermal effects would be felt through the system melt-crucible-thermocouple point as a whole, particularly as they were surrounded by relatively poor conductors. To ensure this and if possible increase the sensitivity, a cylindrical container of alundum was constructed to fit the crucible. The melts, however, were now so small that only the largest points showed up at all on the inverse rate curves, and only the solidus lines of the diagram could be fixed. Nevertheless this was by far the most promising of all the devices tried. Such points as were obtained after the first curve were always repeatable, and the melts appeared very pure ~~pure~~ in their natural colours, which were only now seen for the first time. Chemical analysis failed to show any evidence of change of composition, or of contamination.

The problem was to find a method of greater sensitivity, by which complete curves for these small melts could be obtained.

FIG. 3.



ALUNDUM CONTAINER AND METHOD OF INSERTING CRUCIBLE AND BLANK.

This was finally achieved by using a differential molybdenum-tungsten-molybdenum thermocouple , and after one or two preliminary trials a technique was developed, which was used almost unaltered for the complete investigation.

A cylindrical container of alundum was constructed as shown in Fig. 3, having two recesses side by side just large enough to hold a molybdenum crucible, and a blank of the same material. One of the points of the differential couple, and that of the temperature recording couple were bound to the crucible with molybdenum wire. The other point of the differential couple was bound to the blank. The differential couple was connected directly, via the usual cold junction, to a galvanometer, deflections being indicated by a lamp and scale. The temperature couple leads were, of course, connected to the Tinsley potentiometer as before. Readings of the differential deflections were taken simultaneously with readings of the temperature couple. In some cases a simplification was introduced in that one of the molybdenum wires was used to serve for both couples, so that only three wires came from the furnace. This was found undesirable as a general practice, however, owing to the necessity of preserving the calibrated sample of wire as long as possible, and it entailed the use of calibrated wire for both of the molybdenum leads. Usually uncalibrated molybdenum wire was used for the differential.

The temperature recording thermocouples used throughout were calibrated (1) up to 1050°C against a known chromel-alumel thermocouple, (2) by taking heating and cooling curves for "Armco" iron up to the melting point, and thus obtaining the A_4 point, 1402°C, and the melting point, 1530°C. A check was got by calculating the equation of the curve from the values obtained by the first method and verifying that the iron points lay on it. (This equation is of the form $y=ax^n$, where y represents the thermocouple reading in millivolts, and x the temperature in degrees Centigrade. n is then approximately 2 in most cases.) Several thermocouples have been calibrated by this method and the agreement between them has always been very close.

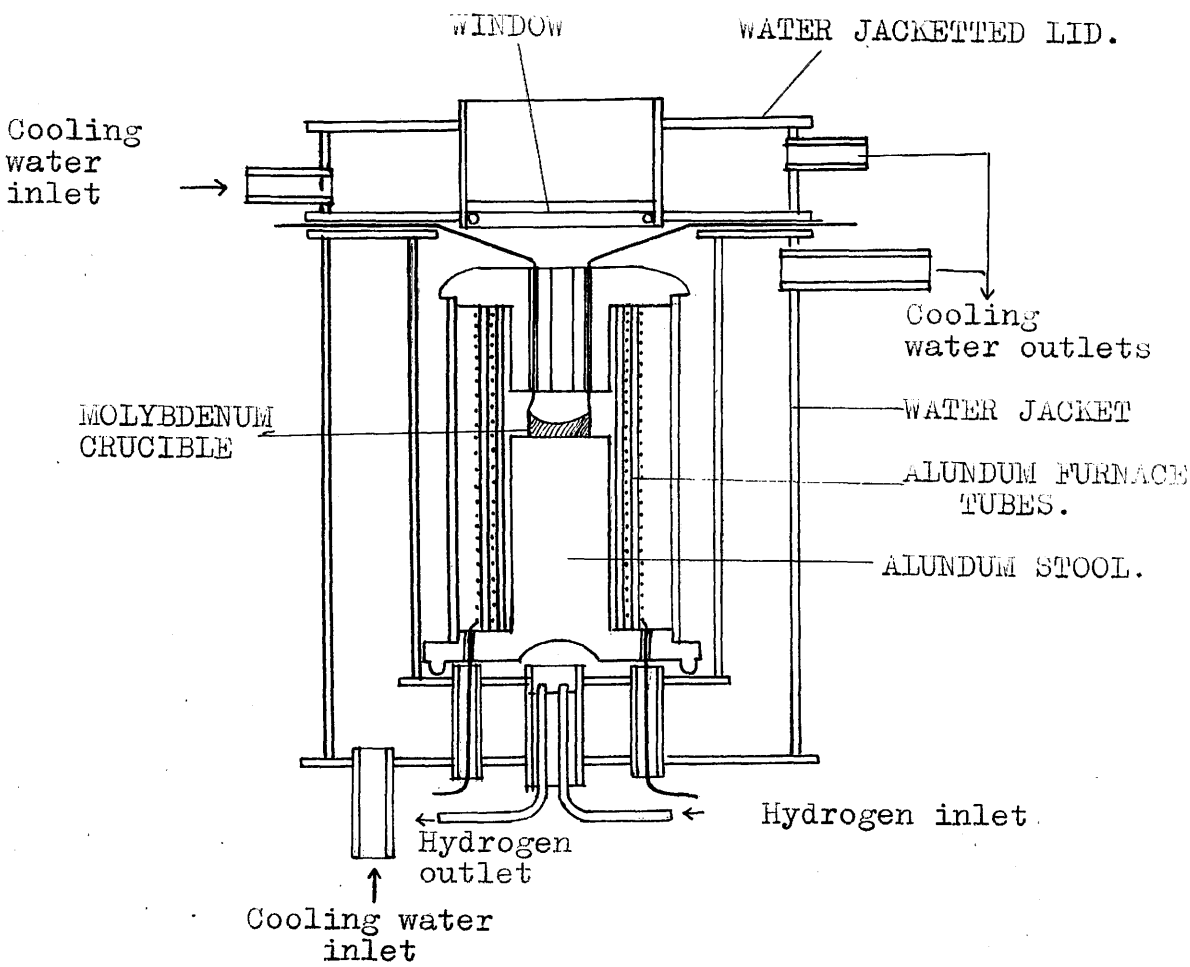
Optical Examination of the Melts for the Identification of Phases.

Using the small molybdenum crucibles described above, it was impossible, short of sectioning the crucibles containing them, to obtain the melts in a form sufficiently massive to permit of polishing and examination by reflected light. The cost of sacrificing a crucible for every melt would have been considerable, so it was necessary to remove the melts by some means. It was found that the only possible method was to chip out a little by percussion, or, alternatively, to make use of a mechanical drill. The material was then obtained in the form of fine fragments. That remaining in the crucible was removed by a combination of fusion in sodium carbonate, and boiling in concentrated acid, a process which only attacked the crucible to a slight extent.

The method adopted to identify the constituents of the fragments of the melt thus obtained was by measurement of their refractive indices, using the Becke method.(see any standard text book on Optical Mineralogy), supplemented as far as possible by determination of other optical properties. This method provides no information as to the structures formed in the melts, but on the other hand, as it actually depends on the measurement of what are physical constants of the phases present, it provides more positive information than examination by reflected light, in so far as identification only is concerned.

A series of standard liquids was prepared with refractive indices up to 1.78. For higher determinations standard glasses of sulphur and selenium, prepared as described by Merwin and Larsen[7], were employed.

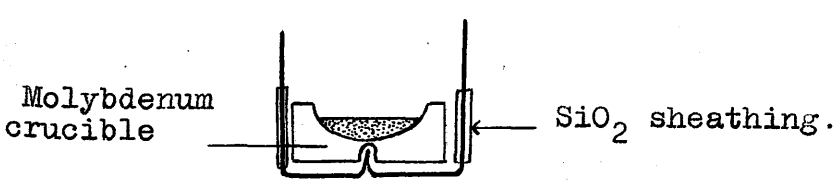
FIG. 4.



VERTICAL SECTION THROUGH HIGH TEMPERATURE MICROSCOPE.

(Actual size)

FIG. 5.



METHOD OF ATTACHING THERMOCOUPLE TO SMALL MOLYBDENUM CRUCIBLE.

The High Temperature Microscope. To assist in the investigation of slag systems, a high temperature microscope was constructed, by means of which fusion and solidification could be observed at high temperatures. Briefly it consisted of a cylindrical water-jacketed container of brass in which the heating element was placed, and a water-jacketed lid, provided centrally with a small window, (See Fig. 4.), above which a microscope could be erected. The furnace unit consisted of two concentric alundum tubes, wound with molybdenum wire .125 millimetres in diameter, and it was mounted vertically inside the container. A stool was provided, as shown in Fig. 4, on which the specimen to be examined could be placed. Melting or freezing could then be observed from outside by means of the microscope. A 35 millimetre objective was found to be very convenient for this purpose, as it allowed of the specimen being placed in the hot zone of the furnace. With the molybdenum winding it was necessary to work in a reducing atmosphere, and provision was made for passing nitrogen and hydrogen (got by cracking ammonia) into the container. A device for clamping down the lid was fitted, and, as packing material between the lid and the body of the container, a ring of plasticene was found very convenient. When the lid was screwed down tightly, this gave a very efficient joint, and , moreover, it was a very simple matter to embed the insulated thermocouple wires in the plasticene without danger of leakage.

A very intense heat was obtainable with these small windings, the highest temperature recorded with this apparatus being just over 1650°C. A shallow crucible of molybdenum was used to hold the melts, and the thermocouple was bound to it as shown in Fig. 5. Only very small weights of melt could be taken, of course. (about .2 grams on the average).

Naturally the temperatures recorded by this means were not expected to be so accurate as those got from heating and cooling curves, and test runs, made with metals in the crucible, indicated in some cases an error of the order of 20 to 30°C. Conditions were, however, definitely worse with metals, as a thin lining

of alundum had to be put over the inside of the crucible to prevent alloying, and, further, the molten metal always formed a spherical drop due to surface tension, and this rose up so high that the upper surface, which was the one under observation, was above the level of the top of the crucible. Hence it is probable that the error with slags in the crucible, never exceeded this figure, and that it was in fact usually smaller. Certainly in many cases the results obtained show remarkable agreement with those which were derived later from heating and cooling curves.

Furnace units wound with platinum were also constructed for the high temperature microscope, and have been used when it was necessary to carry out the heating of the melt in an oxidising atmosphere. These could not, of course,be taken to as high temperatures as the molybdenum windings.

The microscope employed was fitted with a glass plate placed at an angle of 45° to the axis of the barrel, in order that light could be reflected down the tube to illuminate the specimen. As a source of light, a carbon arc lamp, fitted with a condensing lens, was found most suitable, a very intense light being necessary to reveal the specimen at high temperatures when glare from the furnace become troublesome. In the neighbourhood of 1000°C the field was clearly illuminated by its own thermal radiations, but at higher temperatures, these became so intense that all differentiation was lost, and external illumination was required. To improve the visibility a moveable slit was inserted between the arc lamp and the reflecting glass plate. By this means only a portion of the field was illuminated at a time and was revealed much more clearly to the eye than when the whole area was illuminated at once. Even with this device, however, accurate observation at temperatures approaching 1600°C was very difficult.

Attempts were made to photograph the field at high temperatures. Preliminary experiments in the neighbourhood of 900°C with pieces of silver foil in the furnace were very successful, and photo-

graphs were obtained both with "panchromatic" plates using the arc lamp to provide illumination, and with "infra-red" plates by means of the thermal radiations from the specimen itself. At higher temperatures and with manganese silicate melts in the crucible no photographs could be got, the reasons being apparently the increased glare at these temperatures, and the lower reflective power of the slag surface.

Preparation of Materials.

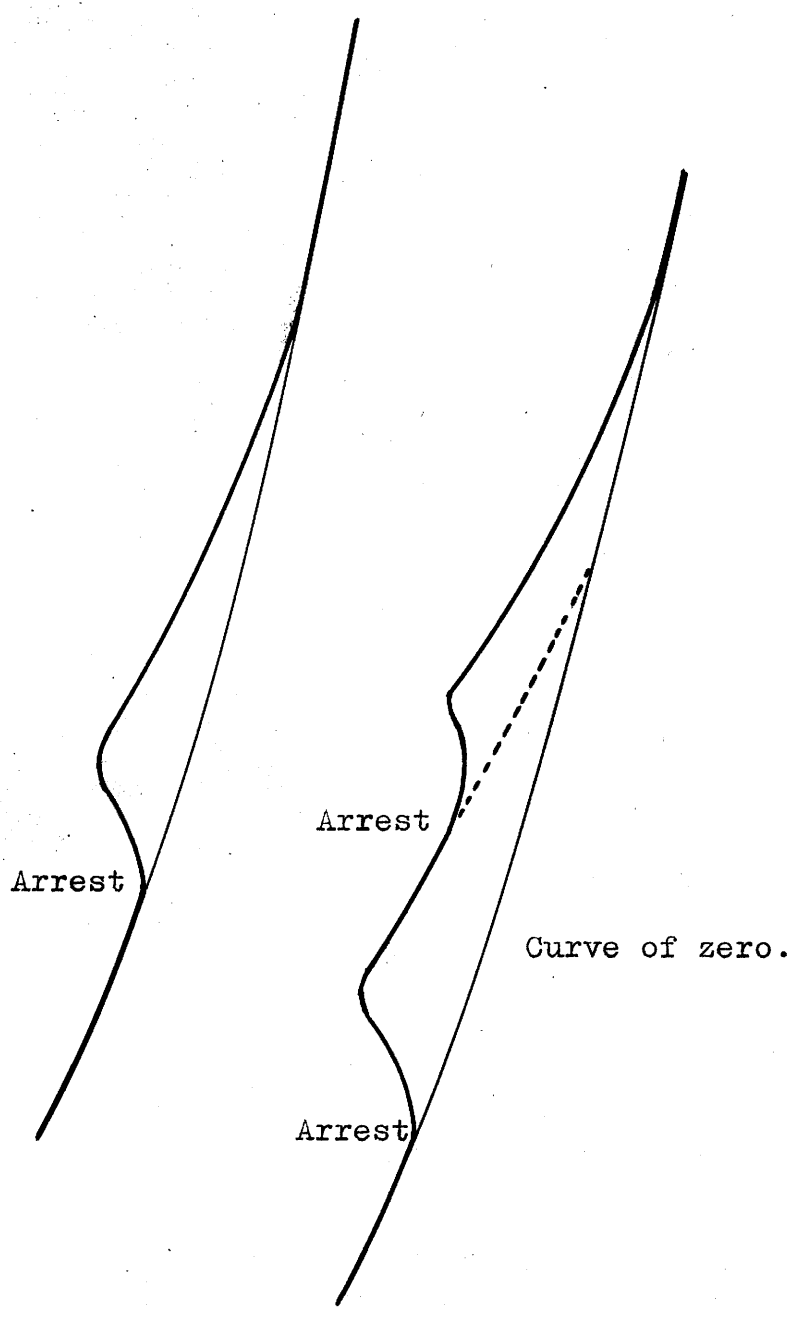
Preparation of MnO. Pure MnO was prepared as indicated by Andrew and co-workers[6] by heating pure recrystallized manganese oxalate to approximately 850°C in vacuo to decompose it, all gases being pumped off as fast as they were evolved. One modification may be mentioned. It was found advantageous, before opening the tube, and after decomposition had ceased, to heat to 1000°C. This rendered the product stable in air. Otherwise it was liable to ignite spontaneously on exposure to air, or to undergo a darkening in the colour due to oxidation. When the above precautions were observed, it was obtained as a dark, olive green powder analyzing pure MnO within the limits of experimental error.

Source of SiO_2. Pure silica sand was employed throughout.

Experimental Results.

Heating and Cooling Curves. The differential heating and cooling curves for this system are reproduced in Figs. 7 to 21. The vertical scale is 1 inch equivalent to .30 millivolts (thermocouple reading), and on the horizontal scale 1 inch represents a deflection of 6 centimetres on the graduated scale of the galvanometer connected to the differential thermocouple. This graduated scale was placed at a distance of 3 feet 6 inches from the mirror of the galvanometer. These curves are reproduced in the untouched condition, including any accidental irregularities occurring, and the method of interpreting each one is fully indicated. In most cases a drift of the zero took place in the differential circuit, and, though the desirability of

FIG. 6.



METHOD OF INTERPRETING DIFFERENTIAL CURVES.

keeping this small is recognized, it has, in most cases, no adverse effects on the value of the curve. Of course in a furnace tube at such high temperatures it is difficult to eliminate local temperature gradients, and this drift was never entirely got rid of, though care was taken to shape the container so that the crucible and blank were symmetrically placed with regard to the winding. Generally three heating curves were taken (the first usually differing widely in contour from the second and third), and two cooling curves, though in some cases three of these were also taken. In taking the earlier curves time-temperature readings were invariably taken simultaneously for purposes of comparison, and to act as a check, but this practice was later discontinued, as it was found to be unnecessary, and only dependable in the case of the larger points. Derived differential curves were also plotted for a number of melts but in most cases no great advantage accrued.

The differential curves were interpreted as follows. The crucible and blank would heat up at the same rate until melting began, when the temperature of the crucible would begin to lag behind that of the blank, and hence the first deviation from zero of the differential galvanometer would that melting had begun, and generally this point, or very closely above it (the position of maximum rate of deviation) has been taken as the point. When melting was complete the temperature of the crucible would once more start to gain on that of the blank, and the deflection would decrease approximately asymptotically till zero was reached again. Hence the position of maximum deviation would occur at or near the conclusion of the heat absorption, and would tend to be prolonged above the true point. Hence it was considered more accurate to take the commencement of the lag as indicating the point. Fig. 6 will indicate the method sufficiently.

In plotting the curves, the ideal zero curve has always been drawn in to assist in the interpretation. This would, theoretically be a vertical straight line, but is rarely so in practice. Several blank runs were actually made with empty crucibles to

determine it, and it was generally of the shape shown, though the exact curvature and slope varied somewhat from heat to heat.

In Figs. 22 to 24 a selection of the ordinary inverse rate time-temperature curves of the same melts is given. It will be observed that these curves only give evidence of the larger arrests.

Discussion of Curves. Curves of MnO: These are reproduced in Fig. 7. Several attempts were made to melt MnO in a molybdenum crucible before success was actually attained. Widely differing figures have been quoted by previous workers. For example, Andrew and co-workers[6] give 1585°C.; Birnbauer and Tude[8] give 1650°C.; Benedicks and Löfquist[9] estimate a temperature of 1700°C or over, while Herty[2] indicates 1610°C. The other workers on this system did not carry their investigations near enough to the MnO end of the diagram to allow of estimates to be made.

In the present instance the first indication of the very melting point of MnO was obtained with the high temperature microscope, when a sample heated to 1650°C showed no signs of fusion. After this two attempts were made in the big furnace one to 1680°C, and the other to 1745°C (maximum temperatures recorded), but in neither case was any evidence of an arrest obtained, and the MnO was found to be still unfused. Another attempt was made, it having been decided to sacrifice the furnace if necessary, and this time success was achieved, although the first curve was not properly completed as the large deflection produced was mistaken for an accidental drift of the zero such as sometimes occurred near the upper limits of the furnace. A second curve was, however, sufficiently completed to show the point. On cooling no very definite points were obtained, due probably to the highly viscous nature of the molten material causing undercooling. Naturally the furnace suffered considerably during this run. The alundum showed signs of slagging, and a new sleeve had to be constructed.

On examination it was seen that the MnO had obviously been melted, although traces of the original outline imposed by the

100% MnO.

HEATING AND COOLING CURVES.

DIFFERENTIAL METHOD.

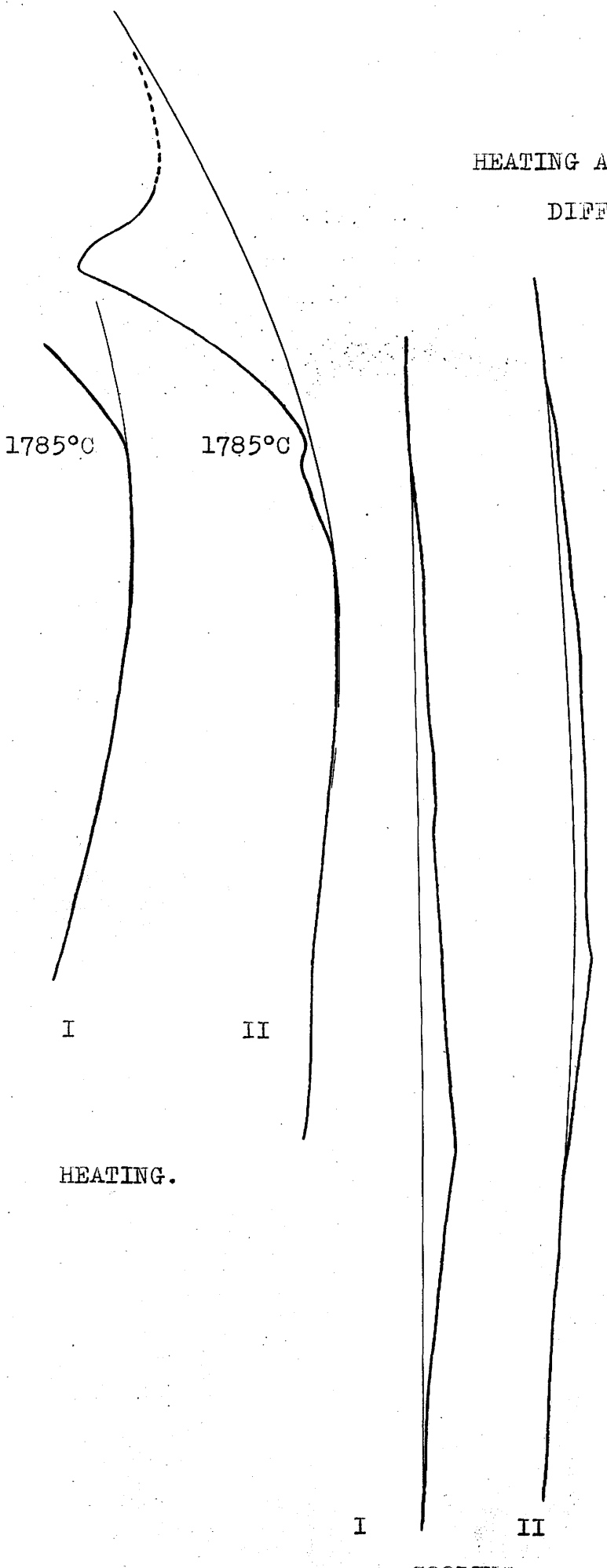


FIG. 7.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2: 8
MnO : 92

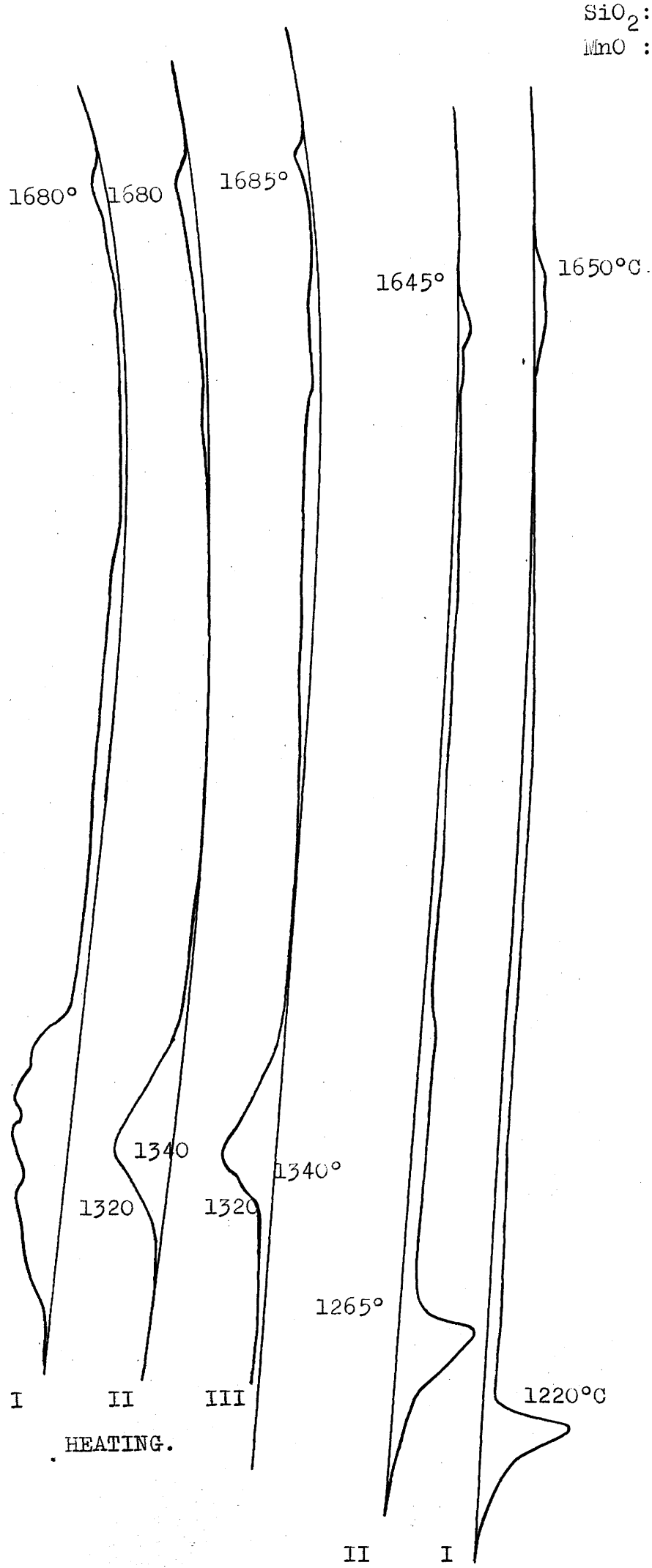


FIG. 8.

HEATING AND COOLING CURVES -

DIFFERENTIAL METHOD. SiO_2 : 18.
MnO : 82.

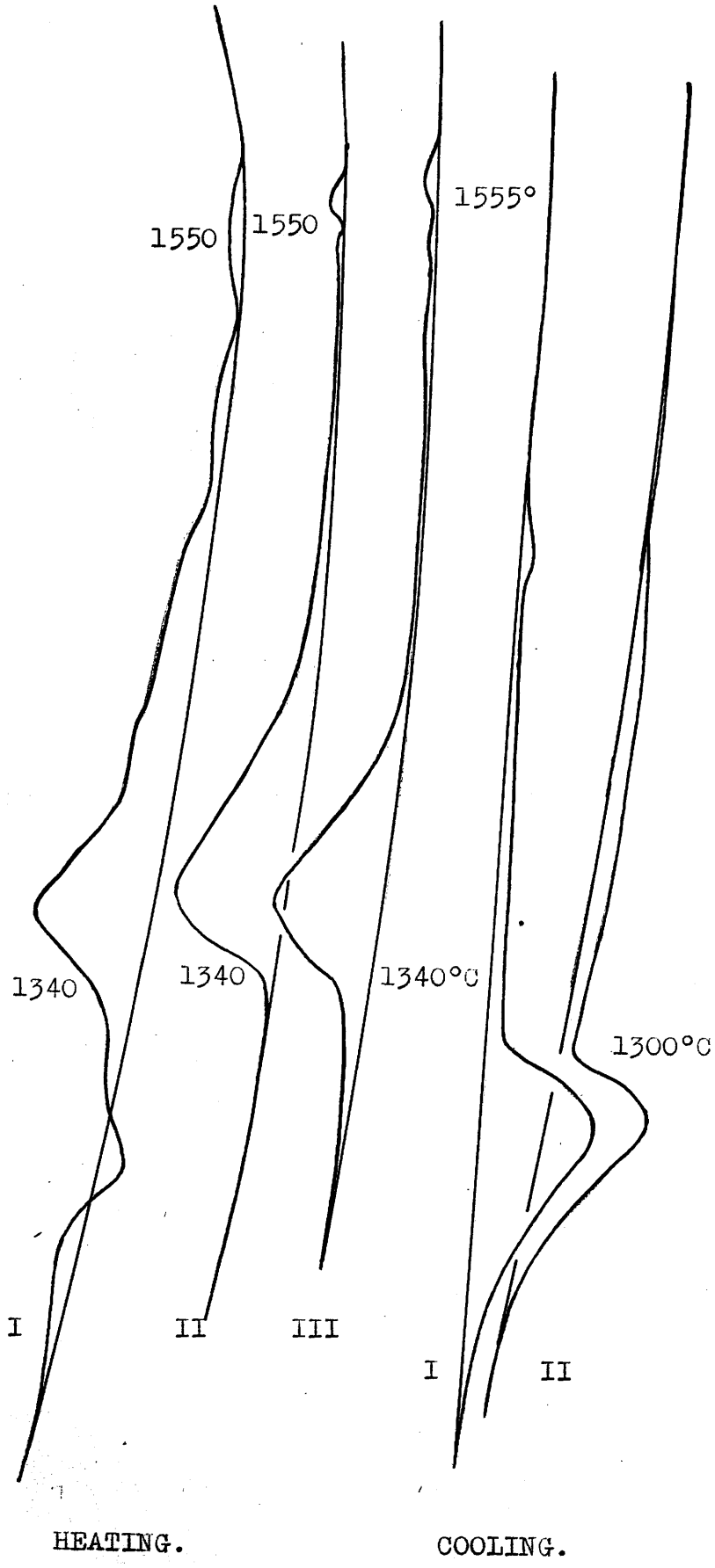


FIG. 9.

HEATING AND COOLING CURVES -

SiO_2 : 32.
MnO : 68.

DIFFERENTIAL METHOD.

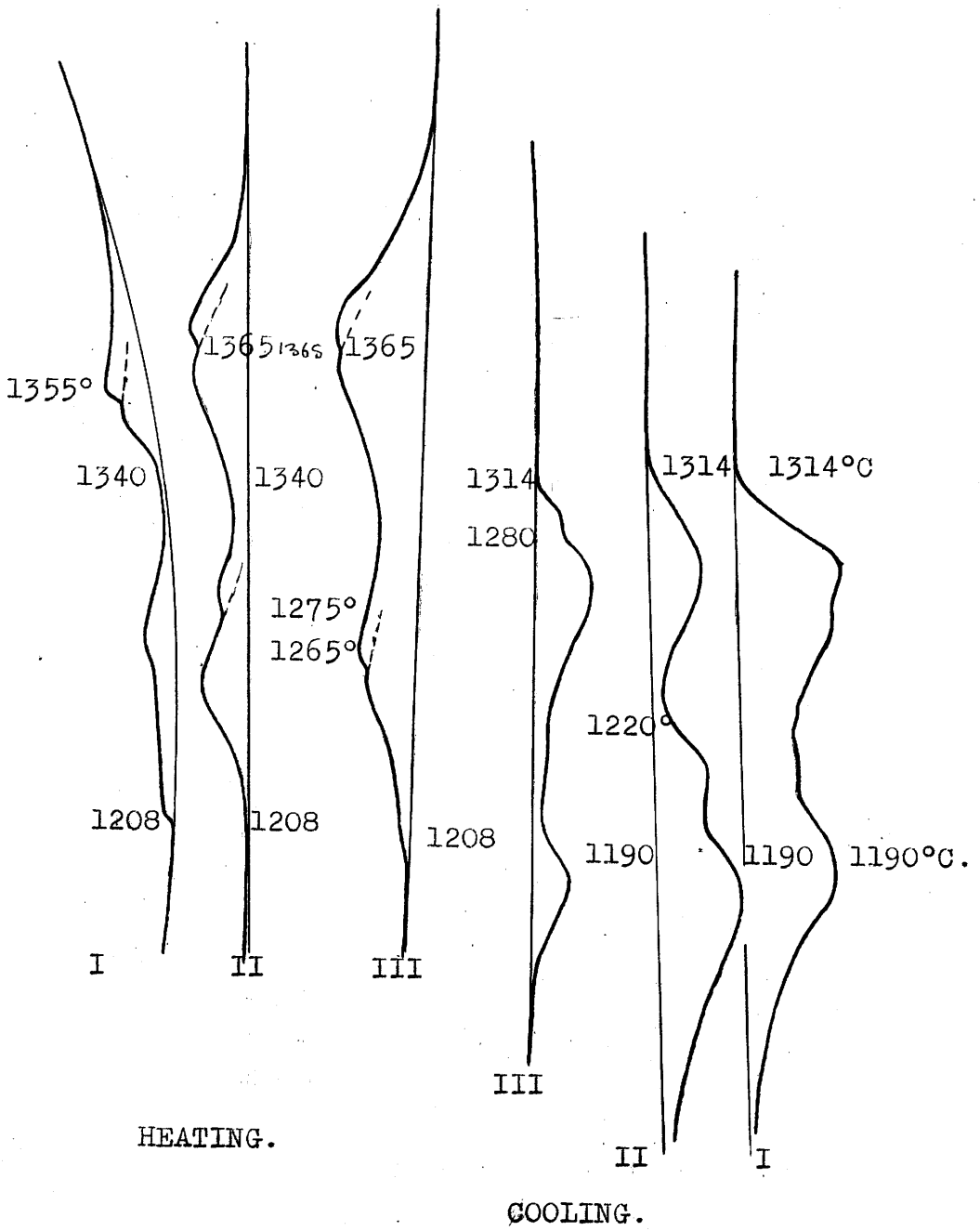


FIG. 10.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 36.
MnO : 64.

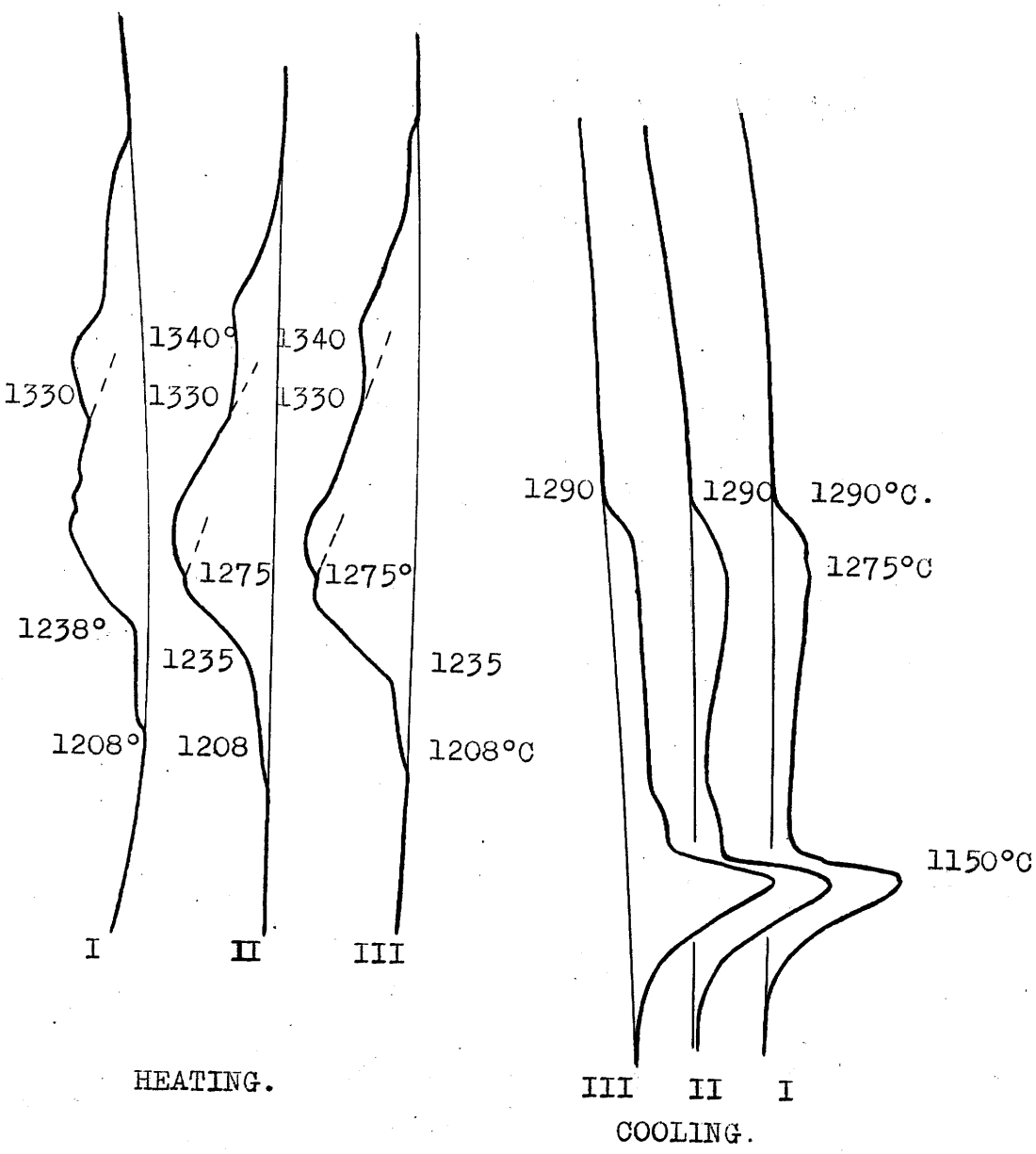


FIG. 11.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 40.
MnO : 60.

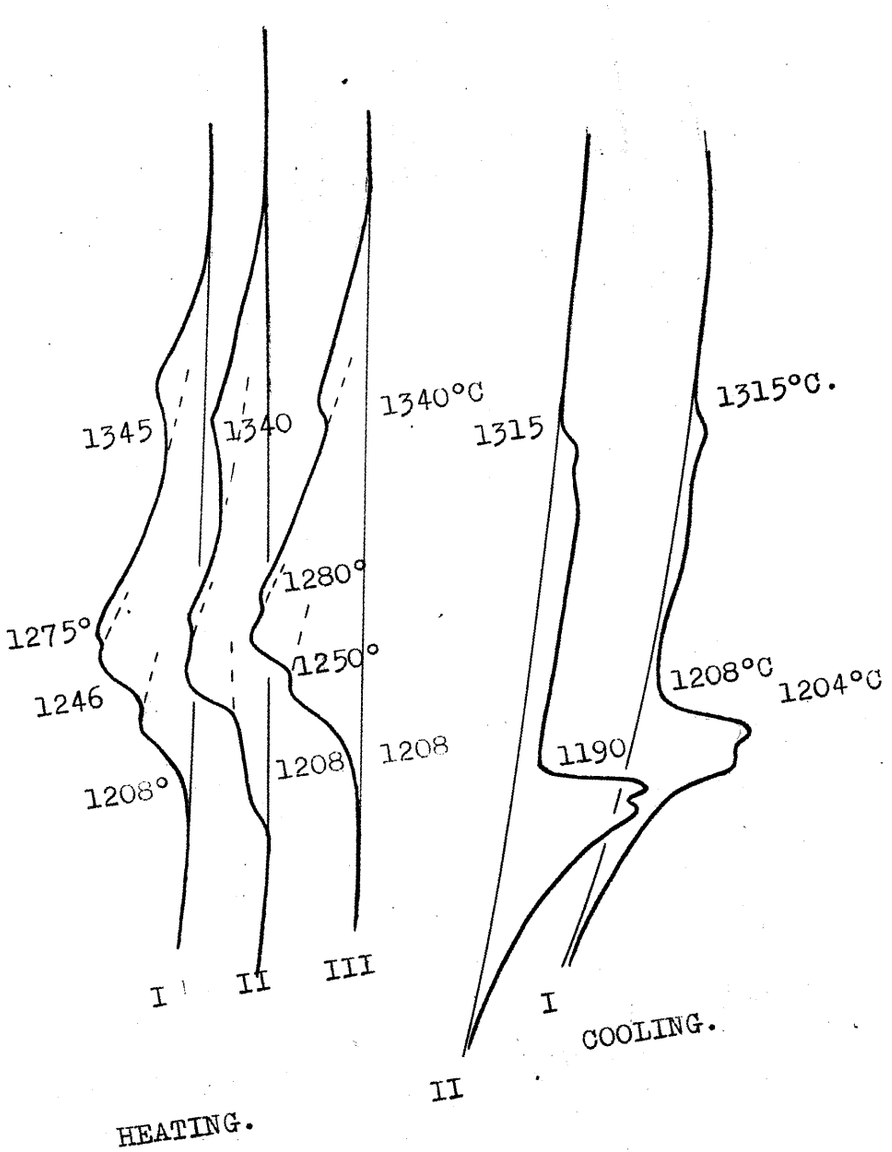


FIG. 12.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 42.5.
MnO : 57.5.

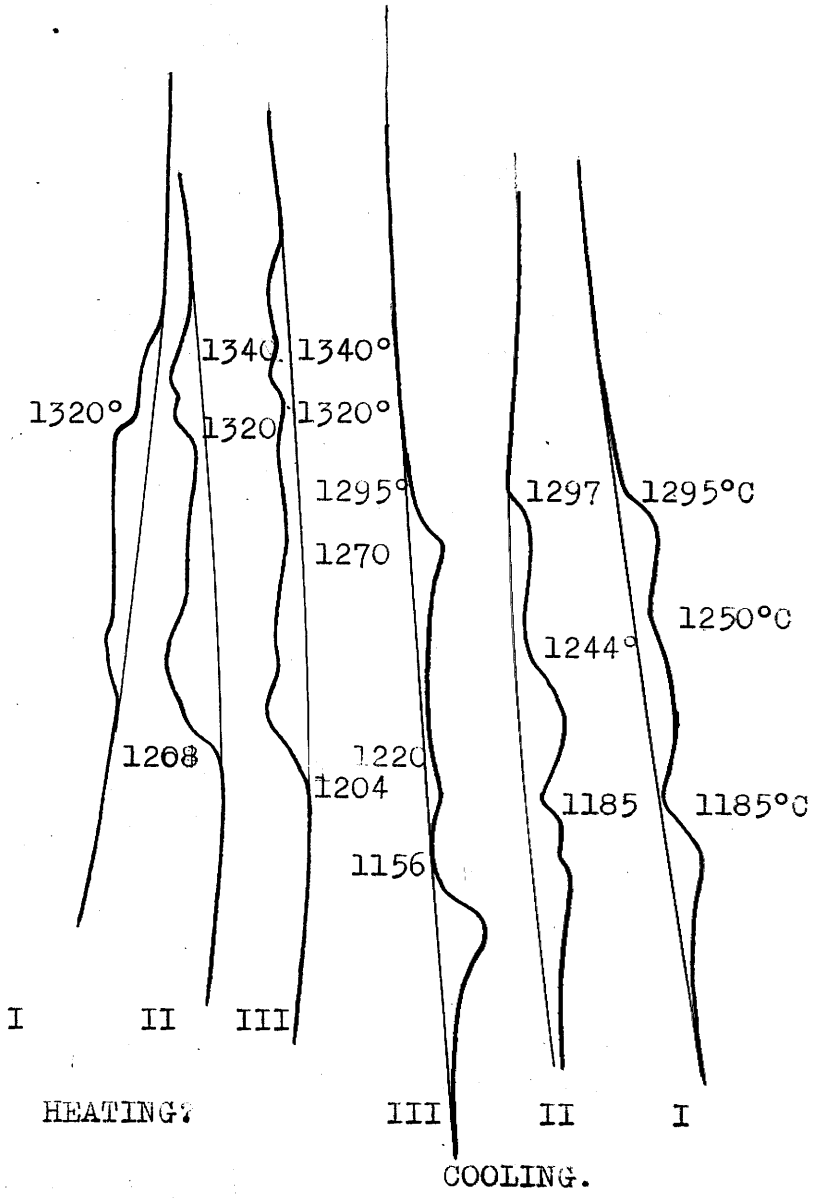


FIG. 13.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 45.8.
MnO : 54.2.

(Rhodonite)

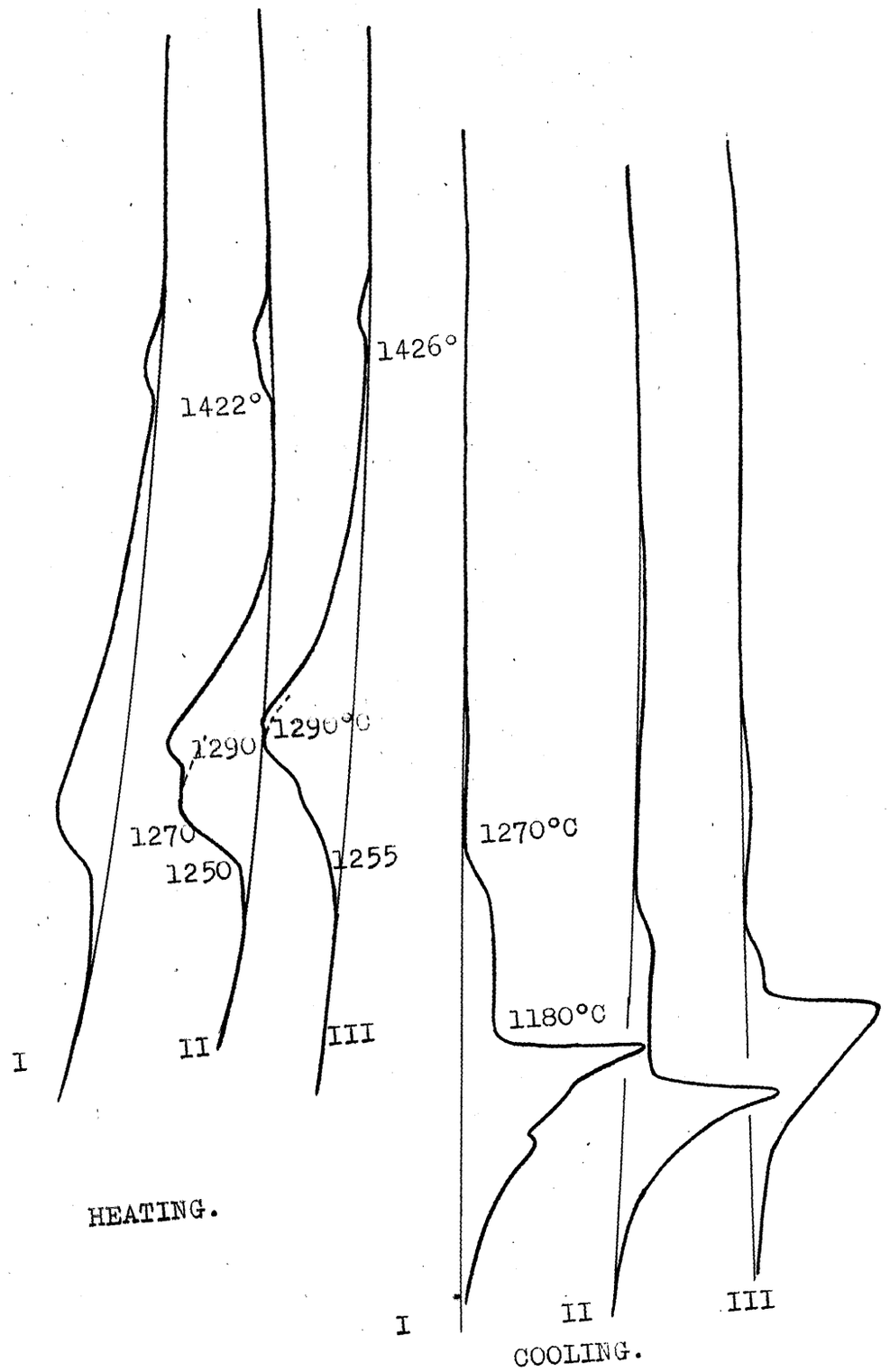


FIG. 14.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 47.5.
MnO : 52.5.

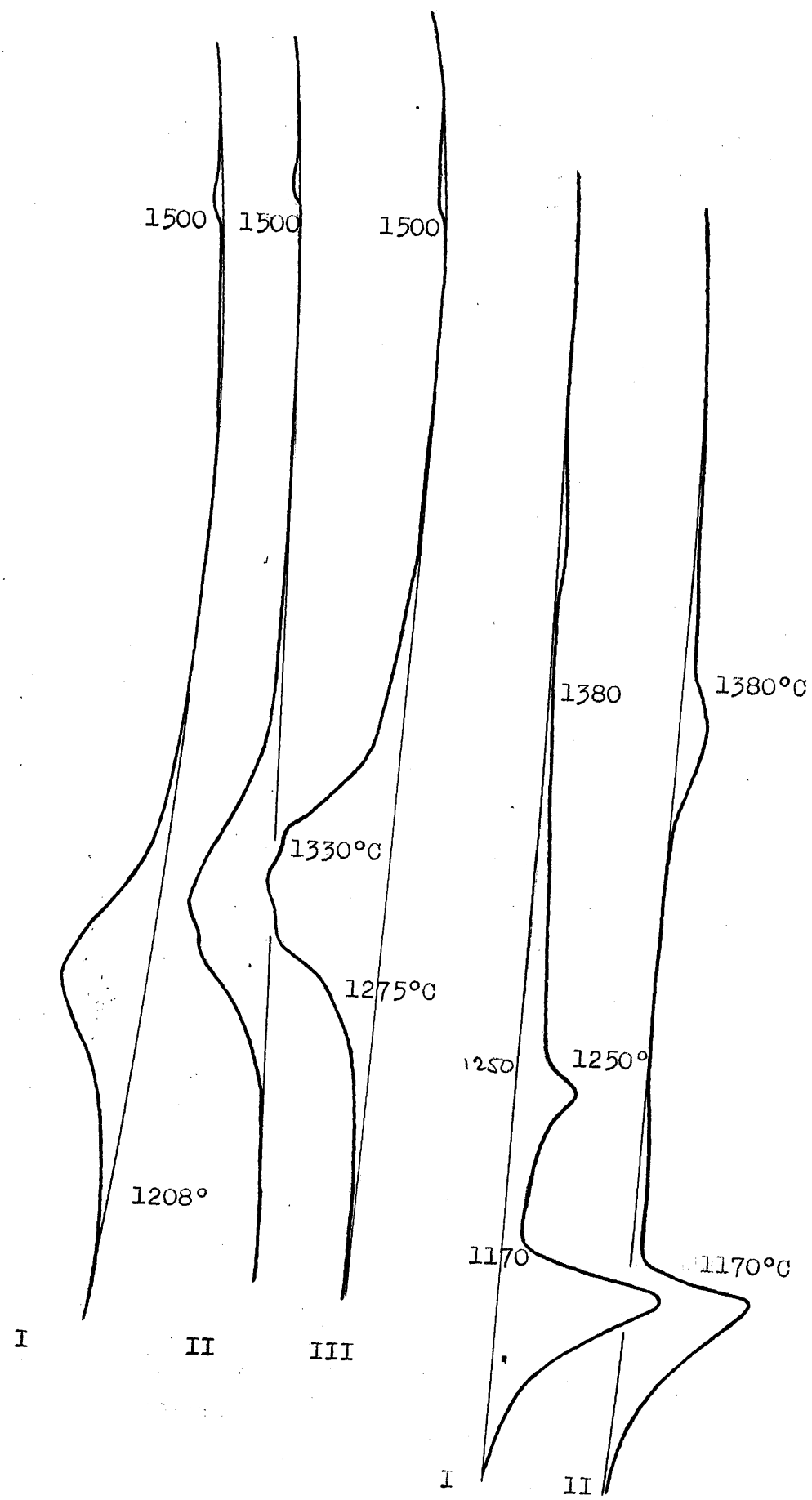


FIG. 15.

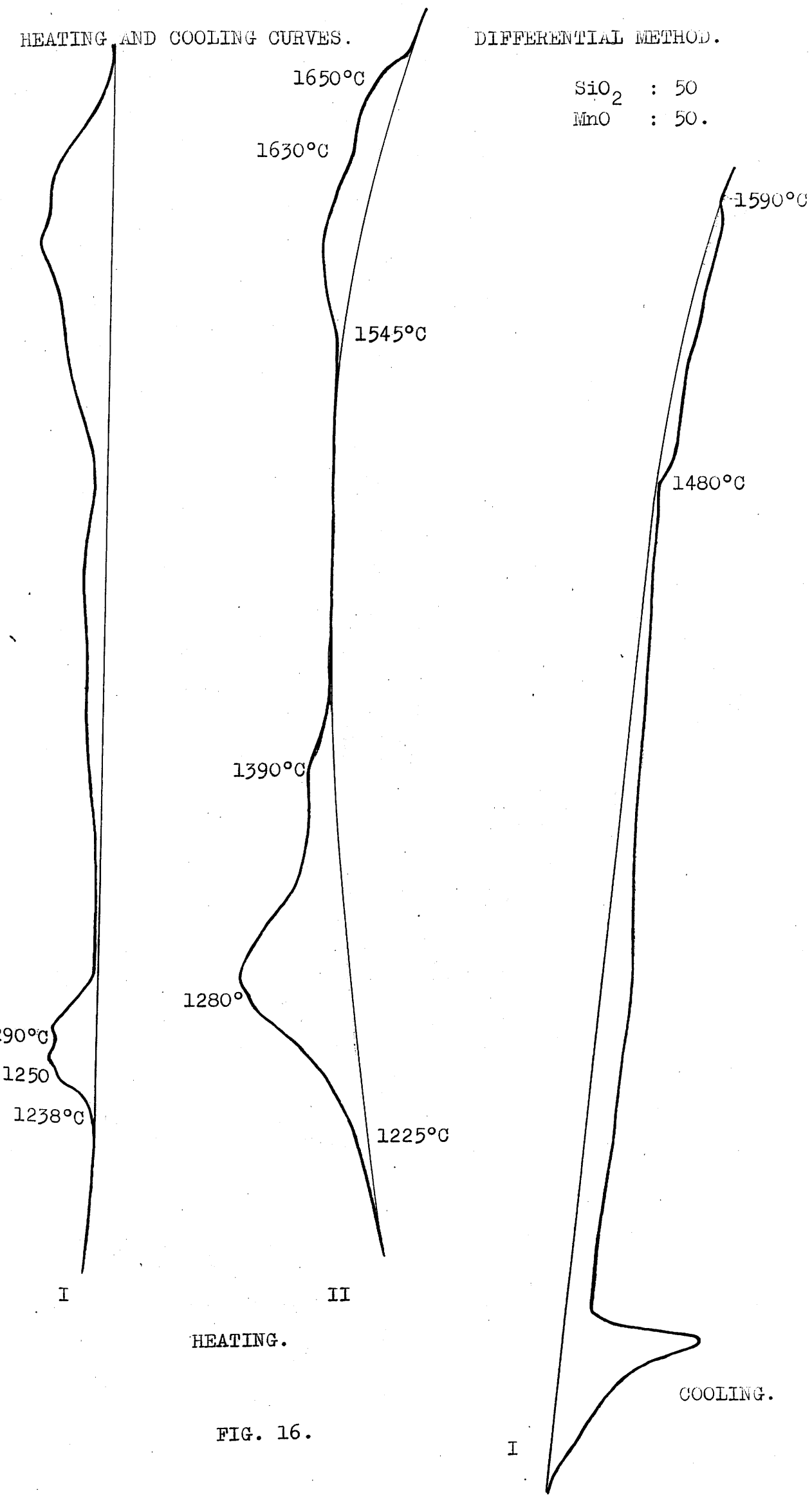

HEATING AND COOLING CURVES.
DIFFERENTIAL METHOD.
SiO_2 : 50
MnO : 50.
1650°C
1630°C
1590°C
1545°C
1480°C
1390°C
1280°
290°C
1250
1238°C
1225°C
I
II
HEATING.
COOLING.
I

FIG. 16.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

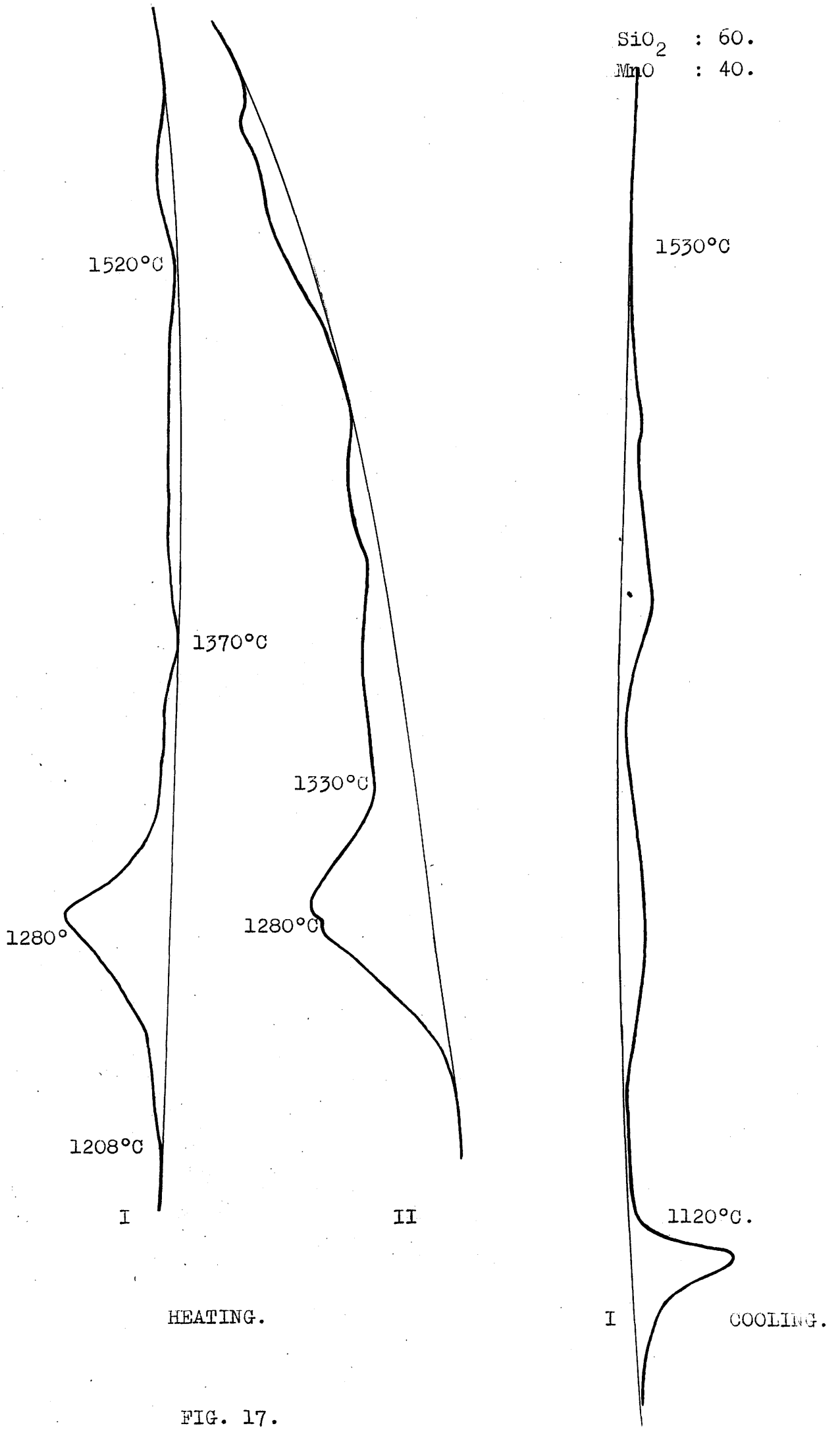


FIG. 17.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 75.
MnO : 25.

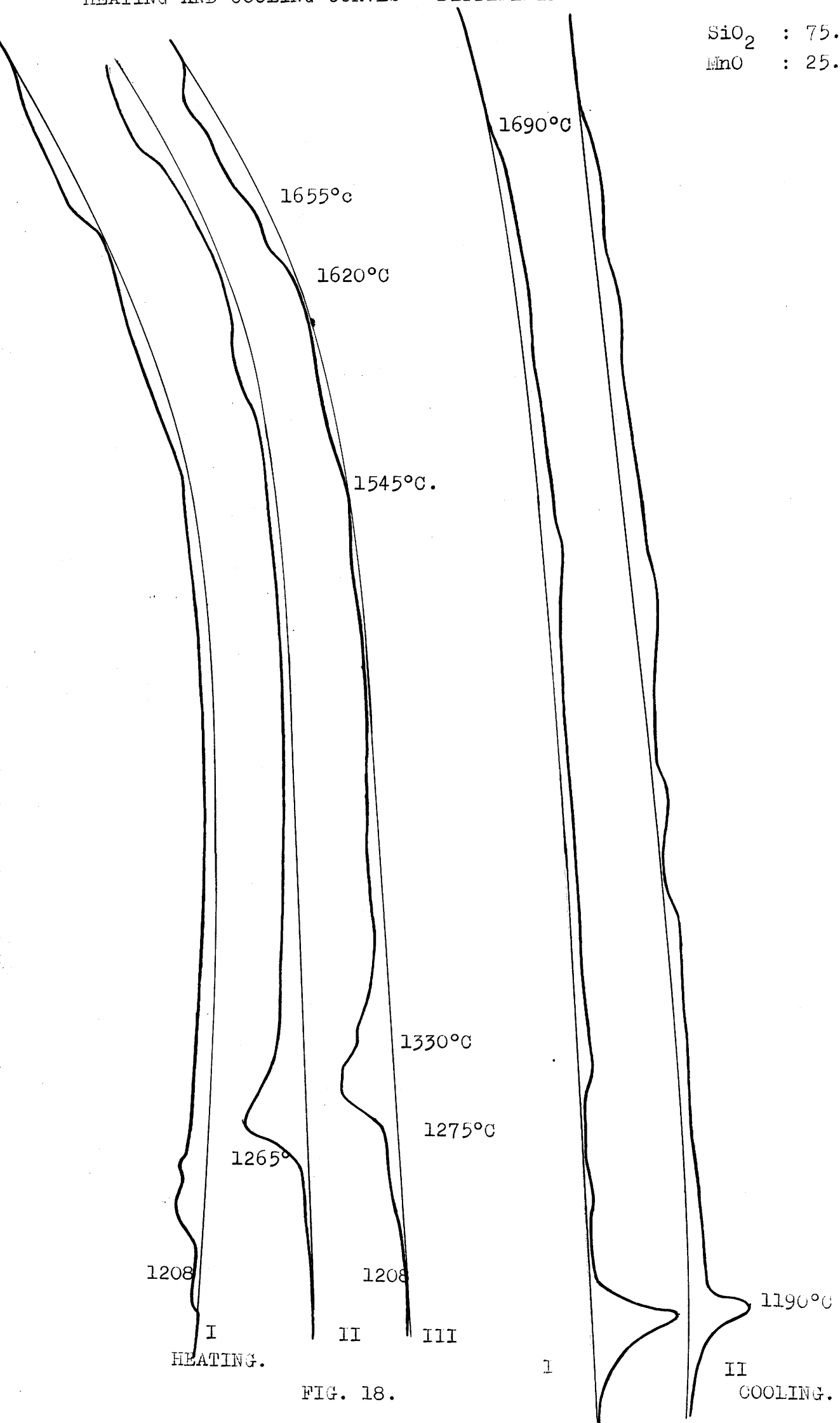


FIG. 18.

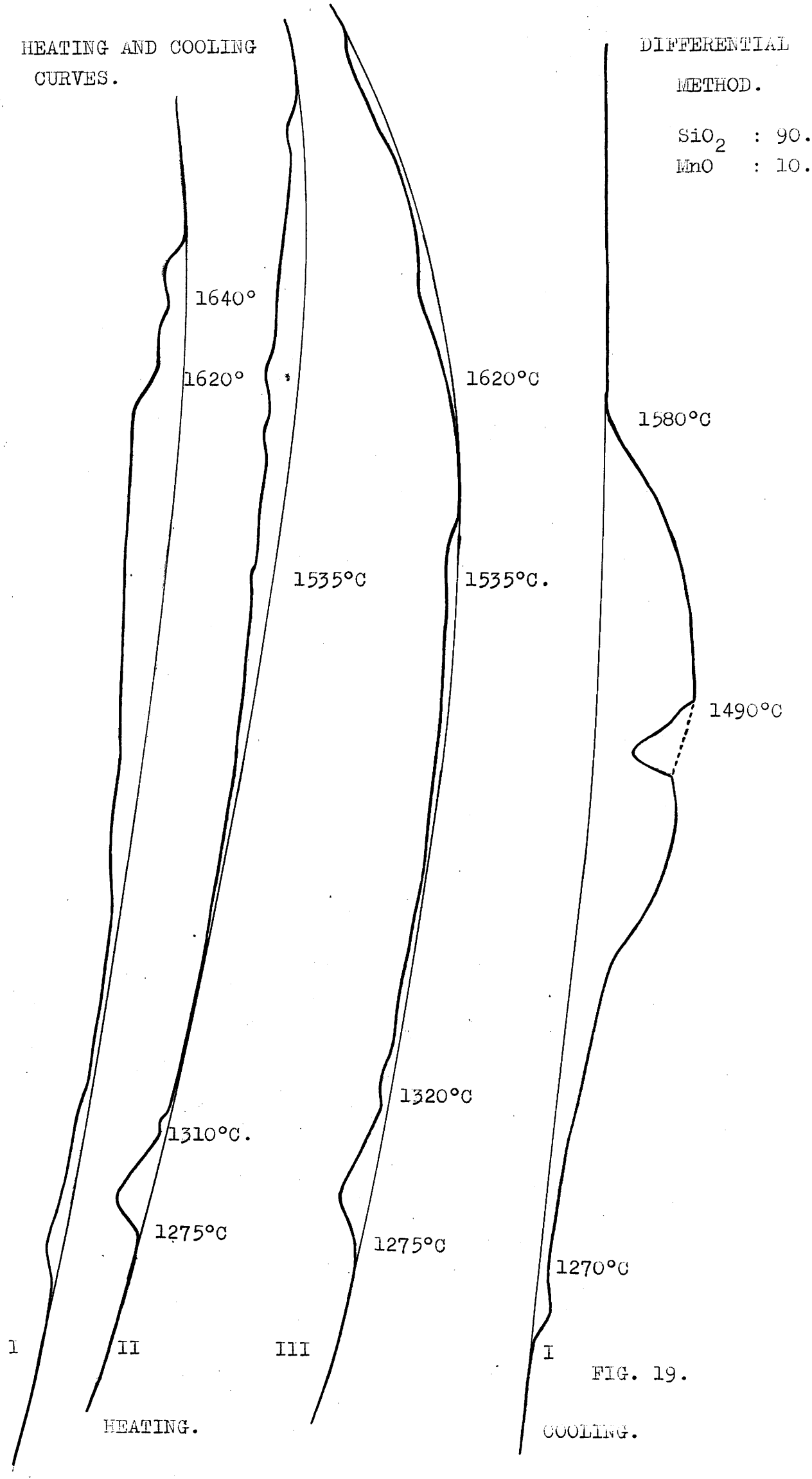

HEATING AND COOLING CURVES.
DIFFERENTIAL METHOD.
SiO_2 : 90.
MnO : 10.
1640°
1620°
1620°C
1580°C
1535°C
1535°C.
1490°C
1320°C
1310°C.
1275°C
1275°C
1270°C
1
II
III
I
HEATING.
COOLING.

FIG. 19.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 97.
MnO : 3.

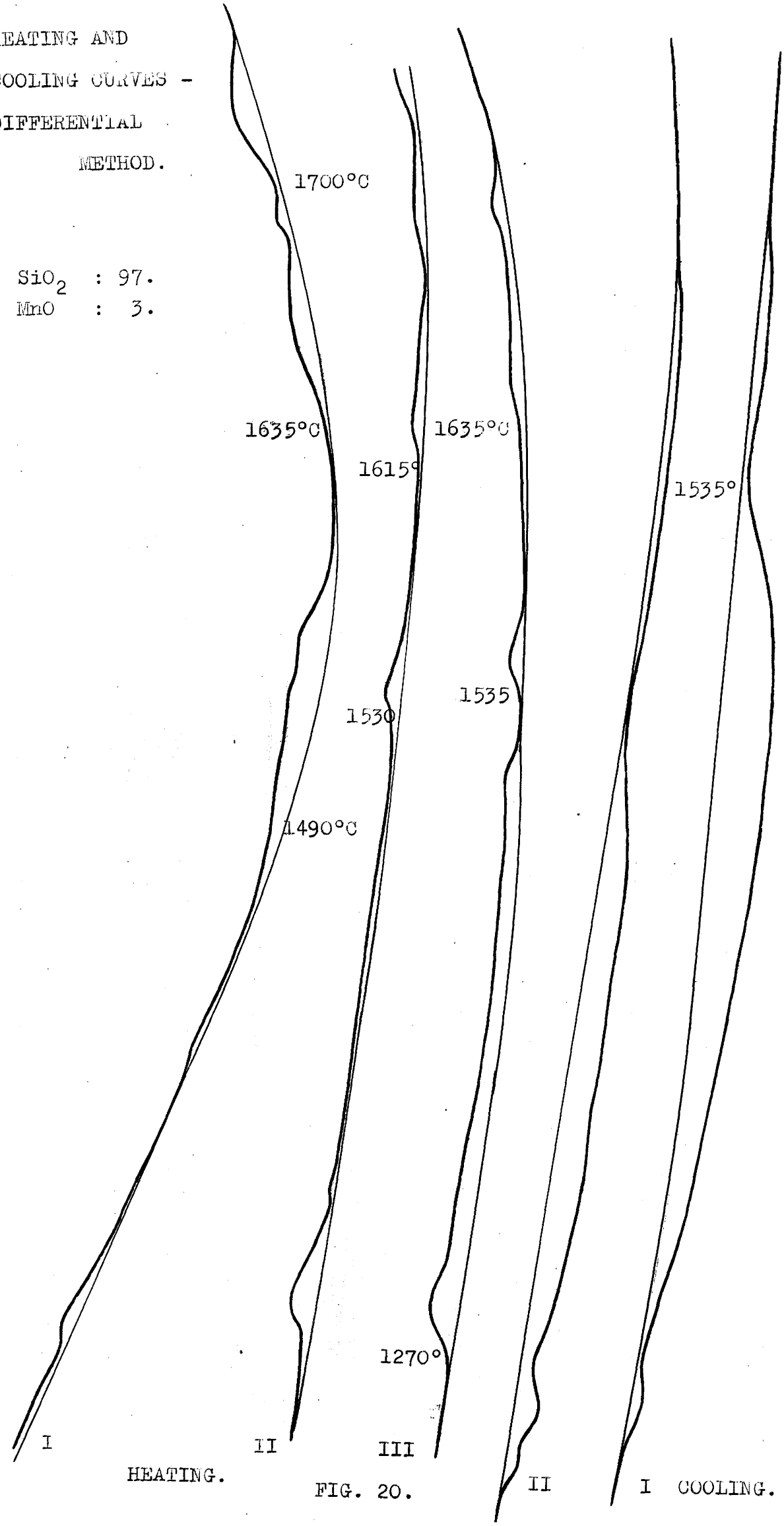


FIG. 20.

HEATING AND COOLING CURVES -

DIFFERENTIAL METHOD.

SiO_2 : 99.

MnO : 1.

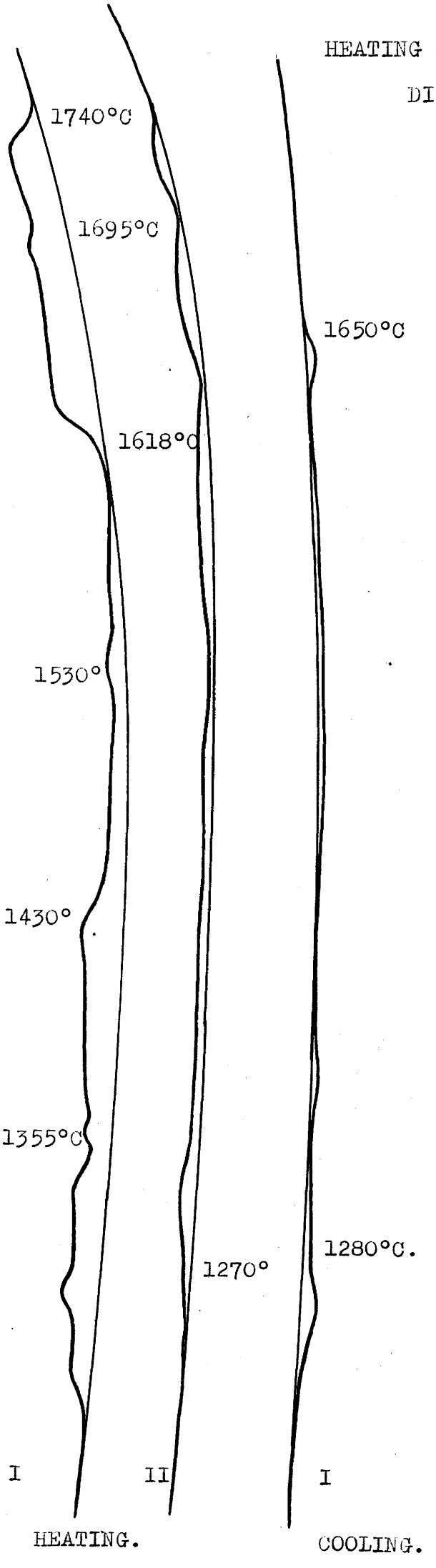


FIG. 21.

INVERSE RATE CURVES.

A selection of the curves taken during the earlier part of the work by ordinary time/temperature methods.

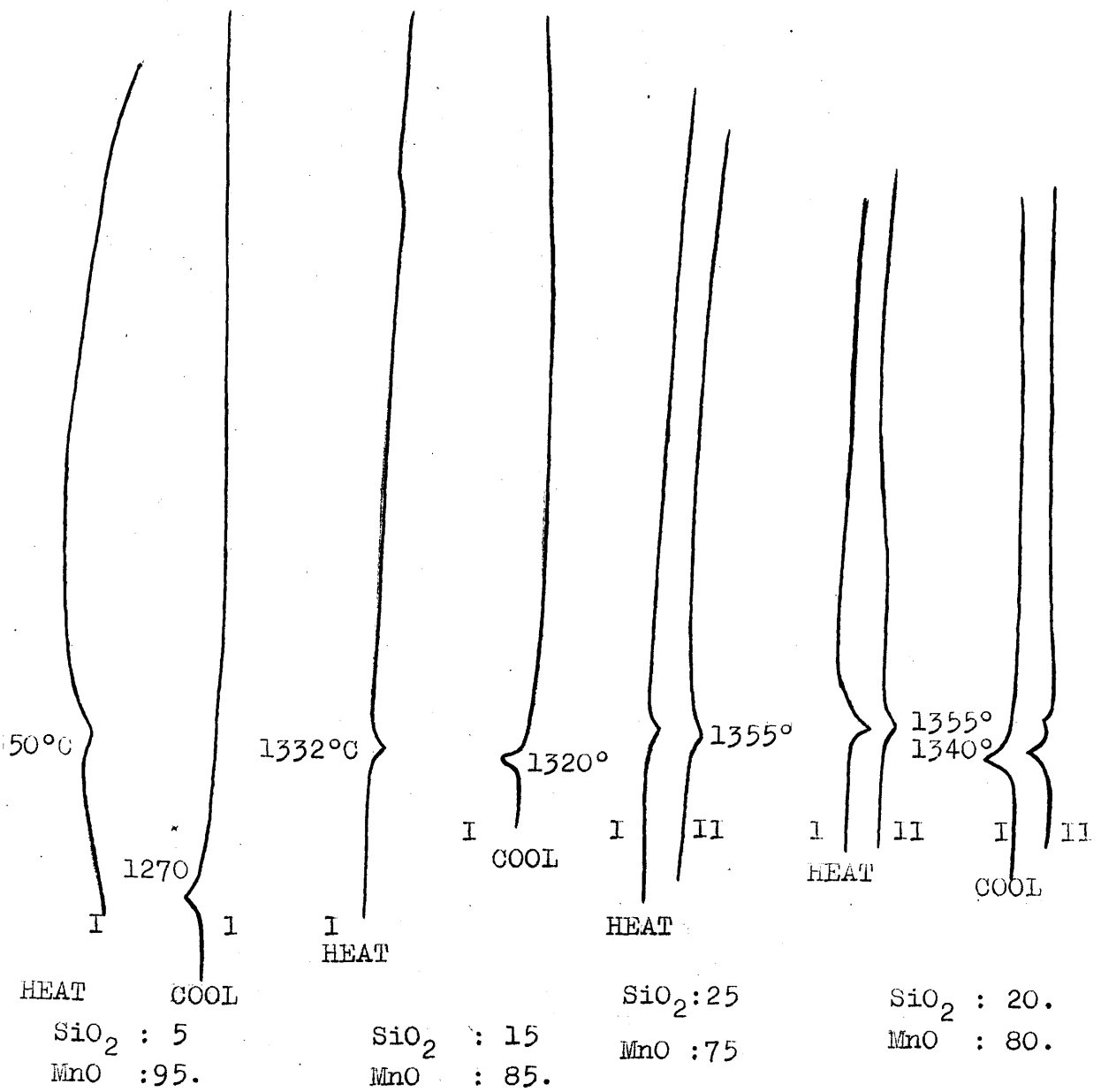
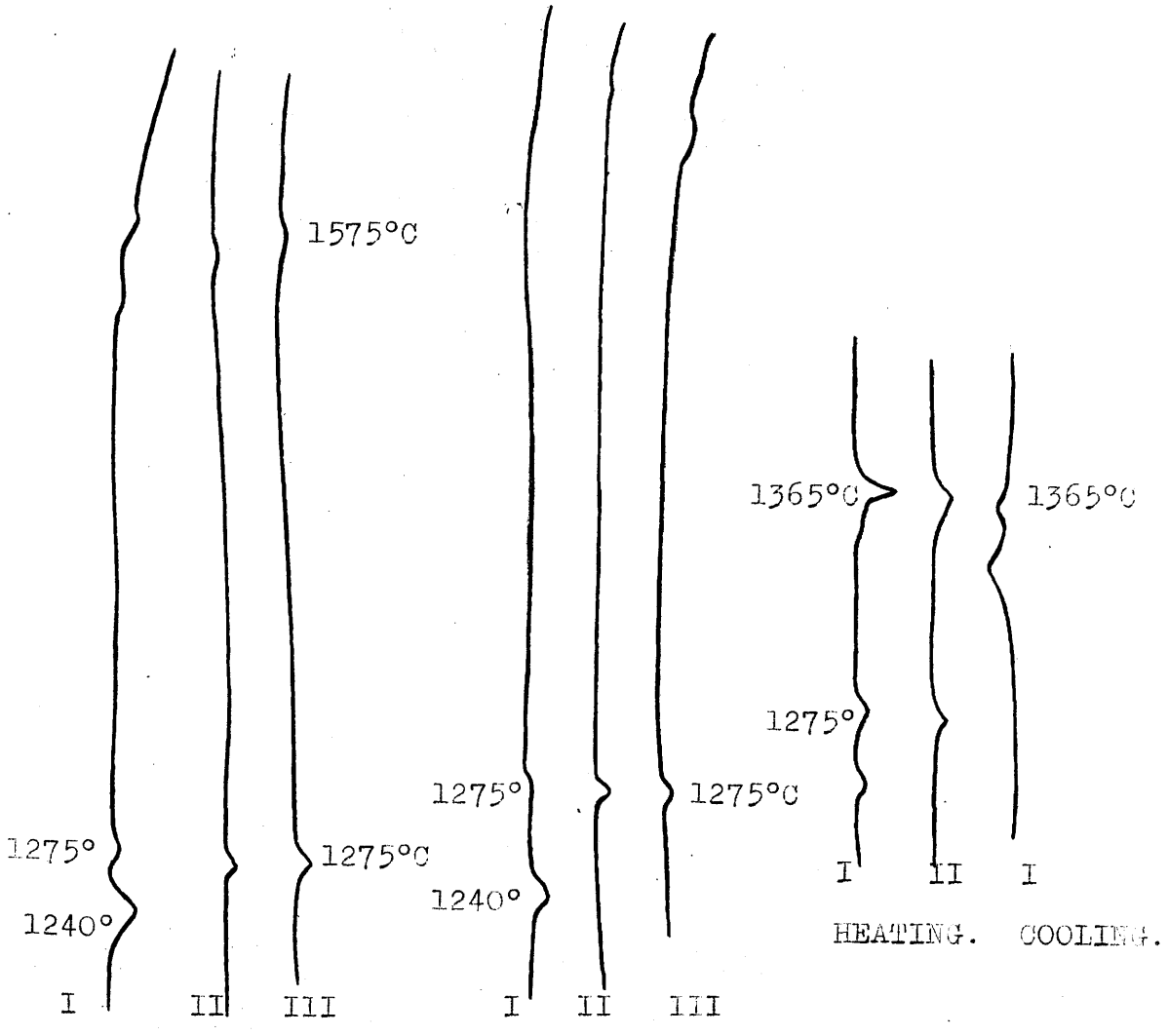


FIG. 22.

INVERSE RATE CURVES.



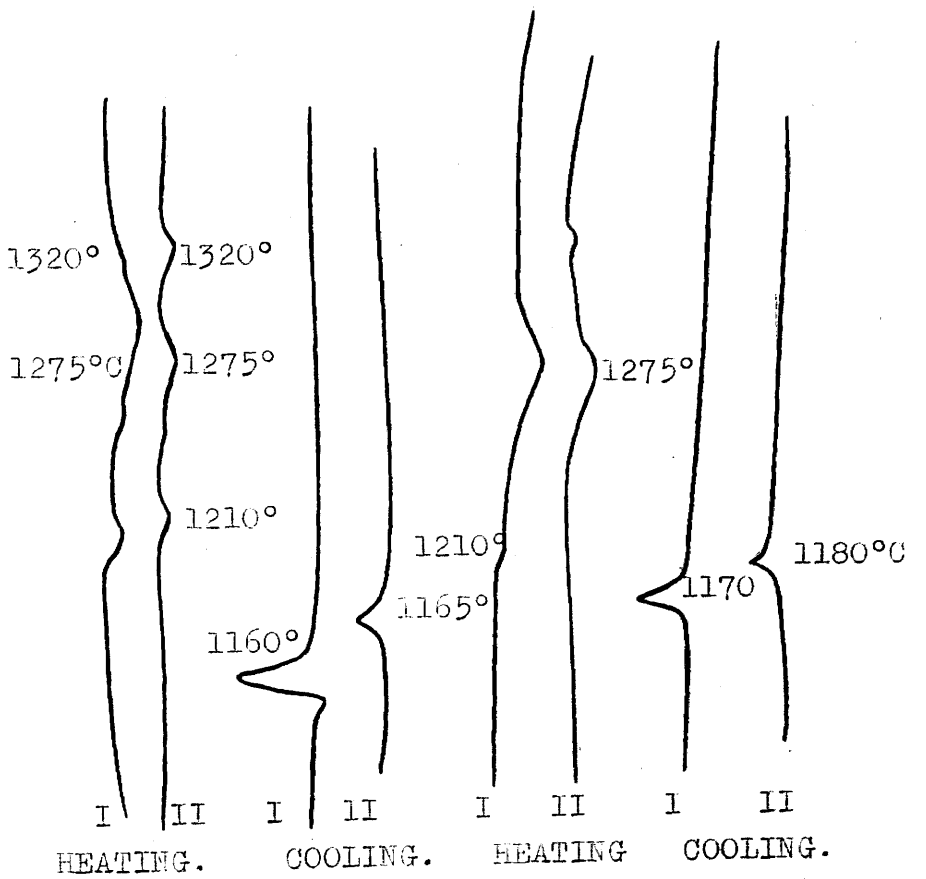
SiO_2 : 50.
MnO : 50.

SiO_2 : 60
MnO : 40.

SiO_2 : 33.
MnO : 67.

FIG. 23.

INVERSE RATE CURVES.



SiO_2	: 44.	SiO_2	: 45.8.
MnO	: 56.	MnO	: 54.2.

FIG. 24.

shape of the crucible could still be detected, showing that it had remained very viscous even when in the molten state. A considerable volume shrinkage had also taken place. This was one of the few melts which could be got from the crucible in a lump suitable for polishing and examination by reflected light, and it was found to consist of a mass of homogeneous polygonal grains of a dark green colour, providing definite evidence that melting followed by crystallization had taken place. It is of interest to note that a time-temperature curve taken some time previously with MnO in an alundum crucible gave a point at 1585°C the temperature quoted by Andrew and co-workers[6].

Remaining Curves: The other curves for this system are shown in Figs. 8 to 21. When SiO_2 is added to MnO in increasing amounts a point appears at 1330 to 1340°C, and this remains constant over a considerable range of SiO_2 content. This point apparently indicates the occurrence of a peritectic reaction, the compound tephroite ($2MnO.SiO_2$) dissociating on heating into free MnO and a SiO_2-rich liquid melt. The determination of the liquidus near the MnO end of the diagram was only made possible by the extreme sensitivity of the differential method. Even so the points obtained were very small, but there seems no reason to doubt their accuracy as they were always repeatable within reasonable limits. Figs. 8 and 9 were obtained with melts lying in this region of the diagram. Curve No. 1 of Fig. 9 is of interest. A distinct heat evolution is shown just after melting had commenced, due, presumably, to the heat of formation of tephroite formed at this temperature from its constituents.

Melts intermediate in composition between $2MnO.SiO_2$ and $MnO.SiO_2$ began to melt at 1208°C (see Figs 10, 11, 12 and 13). This appears to indicate the occurrence of a eutectic between the two compounds tephroite and rhodonite ($MnO.SiO_2$). Almost all of the curves in this region of the diagram present a somewhat puzzling feature in that arrests at 1330°C and 1275°C, the temperatures of peritectic dissociation of tephroite and rhodonite respectively, continue to appear even in the case of melts in which these materials should

have been present only in the fused state at these temperatures. These anomalous points also appeared in the earlier time-temperature curves and led to considerable confusion when attempts were made to interpret them. The explanation is somewhat obscure, unless some form of segregation or liquation were occurring, resulting in the formation of both of these compounds in the massive state together with the eutectic. Certain of the observations made with the high temperature microscope in this region would seem to indicate the possibility of such an occurrence. When once these points had been recognized, the interpretation of the curves in question presented no difficulty. With 32% of SiO_2 (Fig. 10) melting begins at 1208°C, the eutectic temperature, and is continuous, with a suggestion of the rhodonite dissociation at 1275°C, till 1330-1340°C when tephroite dissociates, and above this, so close that the two tend to run together, comes another point, evidently the liquidus. The cooling curves confirm this, there being evidently two points close together at the top. With 36% of SiO_2 (Fig. 11) the tephroite point still occurs (though the mass should be molten at this temperature), but it is much smaller. A large point at 1235°C now follows closely on the first deviation at 1208°C, and is continued over the dissociation temperature of rhodonite, which is indicated by a slight bulge. The cooling curves also show these higher points, together with a very pronounced point at 1150°C, which should be compared with the corresponding point on the cooling curves of the 40% SiO_2 melt (Fig. 12). In the latter case the cooling curves obviously show two points close together corresponding to this one (though the degree of supercooling differs somewhat), indicating that the former is very close to the eutectic composition or at least nearer to it than the latter. This was also confirmed by ordinary time-temperature curves taken simultaneously for these melts, which are not reproduced here. With 42.5% SiO_2 (Fig. 13) the eutectic arrest is again pronounced, and there is another point at 1320°C just below what is probably the tephroite point at 1340°C. The rhodonite point is not well developed but there

is sufficient indication of a well developed point in this region on cooling.

The curves for rhodonite(45.8% SiO_2) shown in Fig. 14 show a large point at 1270 to 1290°C, while there is also a small arrest at 1420°C, evidently corresponding with the liquidus, which must therefore rise very steeply in this region.

The curves of Fig. 15 (47.5% SiO_2) show only the merest trace of a deviation at 1208°C after the first heat (due possibly to a slight lack of homogeneity), but a very pronounced point is shown at 1275°C, with a bulge at 1330°C. The position of the liquidus is very difficult to locate, probably because it rises so steeply, but there is a very slight bulge at 1500°C. The cooling curves merely indicate that the liquidus must certainly be higher than 1380°C.

It should be pointed out that, with increasing SiO_2, the points, apart from that due to the rhodonite dissociation, became very sluggish and uncertain, and the same certainty does not attach to this part of the diagram as to the earlier part, at least as far as the liquidus is concerned. From 50% of SiO_2 onwards the curves may be discussed together . Briefly, there is an invariant point at 1270 to 1280°C, which becomes smaller with increase of SiO_2. There is also a more or less uncertain heat absorption at 1530 to 1540°C on most of the curves, which may possibly be due to the rather sluggish tridymite-cristobalite change taking place in the free SiO_2 in presence of MnO (or rhodonite) as a flux. At the rates of heating employed such a change if it occurred at all, would naturally be expected to occur at a temperature rather higher than theoretical. Several of the curves also show what may be points at higher temperatures and from these a more or less tentative liquidus has been sketched in to conform with the probable existence of two immiscible in this region as found by Greig[3].

It was not intended to carry out a run on pure SiO_2, but the melting point of this material was obtained accidentally in taking a melt to over 1700°C, when the silica sheathing on the thermo

couple melted and dropped on to the blank. Thereafter three successive runs showed the point (in the direction of heat evolution by the melt) at temperatures from 1695°C to 1705°C. After that other means other means of insulation had to be employed for very high temperatures.

Observations with the High Temperature Microscope:

The high temperature microscope proved of great value in investigating the system $MnO-SiO_2$, and provided the first incontrovertible evidence of the melting ranges, before the employment of the differential thermocouple. The method employ- was to heat up the specimen while observations were made through the microscope. The current was controlled by two rheostats in series giving very fine adjustment, and the rate of heating could be very accurately controlled. If necessary the temperature could be held stationary to allow changes to take place.

The following temperatures were noted ,

(1) when the first liquid appeared,

(2) when the mass became mainly liquid and lost rigidity of shape, if this took place suddenly as it often did.

(3) when the last traces of floating solid disappeared. This latter could not always be determined with certainty as sometimes the surface was lost owing to the glare, and because the window tended to become coated with a reddish deposit, probably from volatilization of the molybdenum windings. For this latter reason it was not always possible to take records of cooling, but where this was done they have been reproduced. Where several heatings were observed the observations are tabulated. In those cases where the melt was freshly made up from the constituent MnO and SiO_2, the first heats have not been recorded. In general it was found that on these heats no liquid appeared till much higher temperatures than normally, which agrees with what was found in the case of heating curves of such melts. Small amounts were employed but great care was exercised in making the weighings involved, so that the percentages quoted should be reasonably accurate.

Details of the Melts;

100% MnO.

Taken up to 1650°C. No signs of fusion.

91% MnO: 9% SiO_2:

First liquid appeared at 1350°C. Very small in bulk.

At 1610°C solid was still in existence. Could not be followed further owing to glare.

At room temperature the melt appeared dark green in colour, and "sat up" high in the crucible indicating high surface tension.

73% MnO: 27% SiO_2.

Second Heat:

First liquid appeared at 1240°C. Only in very minute traces and in localized areas.

The bulk of the mass became liquid rather suddenly about 1360°C.

The last solid disappeared at 1430°C.

Third heat:

First liquid appeared at 1350°C, when the bulk of the mass appeared to melt.

The last solid disappeared about 1440°C

Evidently the first heating of the constituents had been insufficient to homogeneize the melt and some liquid appeared at 1240°C on the second heating. The melt appeared dark green on removal from the furnace, and possessed high surface tension.

68% MnO: 32% SiO_2.

Second Heat:

First liquid appeared at 1160°C. Only in two small local areas and possibly due to traces of impurity (dust particles, etc.).

The bulk of the mass was liquid by 1280°C. This took place gradually.

The last solid disappeared at 1360°C.

Third Heat:

First liquid appeared at 1200°C.

The bulk of the mass was liquid by 1280-1290°C.

The last solid disappeared at 1345-55°C.

53% MnO: 47% SiO_2.

Second Heat:

First liquid appeared at 1210°C. Only in small amounts.
The bulk of the mass went liquid and the rigidity of shape was lost rather suddenly about 1280°C. Particles of SiO_2 (probably) floating on the top in the form of rosettes.
Between 1455 and 1460°C the amount of floating solid increased.
No further change until 1525°C when all apparently went liquid.

Third Heat:

First liquid appeared at 1205-1210°C. Small amounts.
The bulk of the mass went liquid at 1290°C. Appearence as on second heat.
The surface appeared to set solid about 1440°C. All liquid again over 1520°C.

On standing at just over 1450°C, the solid continued to separate on top, so that the effect did not vary progressively with rise of temperature. Further it was not reversible on cooling. On removal from the furnace the appearance of the surface depended on the temperature to which the melt had been taken; if this were under 1500°C it appeared white probably due to separation of a layer of SiO_2, if over about 1520°C it had the characteristic pink colour of rhodonite.

It is probable that the phenomenon observed here was the solution of the SiO_2 in the flux (rhodonite) and its simultaneous precipation at the surface. The conversion of SiO_2 from one modification to another by means of this mechanism has been observed by many workers. In the present instance the surface layer would almost certainly be at a somewhat lower temperature than the rest of the melt, and such a reprecipitation would be particularly liable to occur. The form of SiO_2 precipitated was most probably tridymite as it tended to take the form of lamellae radiating from a common centre.

52% MnO: 48% SiO_2.

First liquid appeared at 1210°C. A trace.
The bulk of the mass went liquid at 1280°C, but complete rigidity

was not lost till about 1400°C. Observations incomplete.

50% MnO: 50% SiO_2.

First liquid appeared at 1210°C. A trace.(On cooling all appeared solid by 1280°C).

Bulk of the mass went liquid between 1280 and 1320°C.

Crystals on the surface began to increase about 1500°C. All liquid at 1600°C.

As above the appearance of the surface depended on whether the melt had been taken to a temperature high enough to dissolve all the solid.

Discussion of Observations with the High Temperature Microscope.

On the whole the agreement between these observations and the heating and cooling curves is very close. The three melts ranging from 53% to 50% of MnO are of interest, because of the apparent separation of solid at the surface as already described. While the explanation advanced above is very possible, there is also a possibility that it might have been an ordinary liquation effect, caused, for example, by a difference in specific gravity, or it may have been due to surface tension effects, as these melts tended to spread themselves over the surface of the crucible, and being very small, formed a very thin layer. Whatever the explanation a very steep liquidus in this region is probably indicated.

There seems to be a very distinct tendency for segregation to occur in manganese silicate melts. As can be seen from these observations, even melts with SiO_2 present in excess of the rhodonite composition, tended to form small amounts of liquid on passing through the eutectic temperature, in spite of the fact that they had previously been completely fused. The thermal curves provide evidence which seems to support this. Further attempts to observe melts approximately of the eutectic composition were not successful as the materials never appeared completely liquid till temperatures as high, in some cases, as 1330°C were reached. Possibly segregation was the cause.

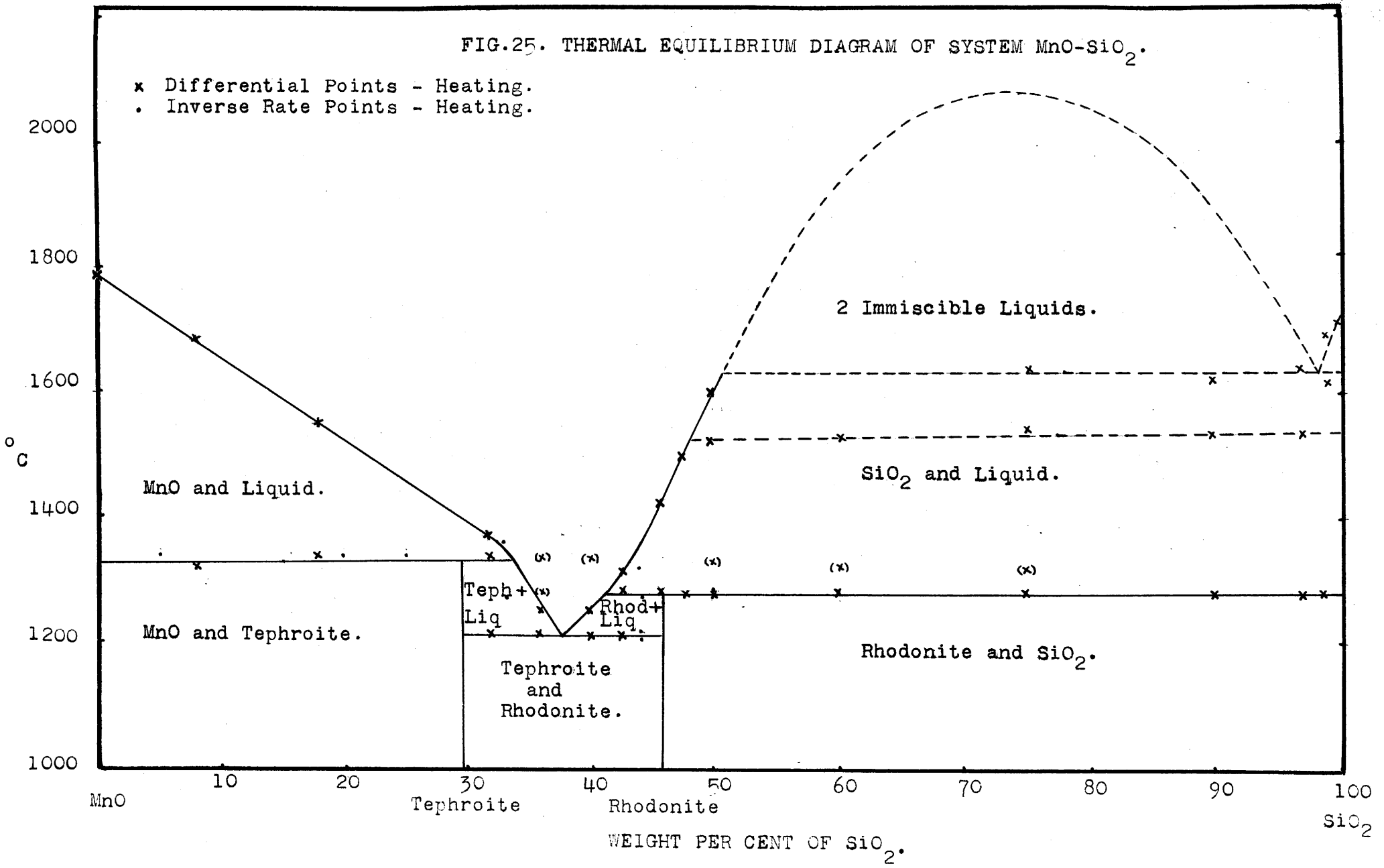


FIG.25. THERMAL EQUILIBRIUM DIAGRAM OF SYSTEM MnO-SiO2.
× Differential Points - Heating.
· Inverse Rate Points - Heating.
2000
1800
1600
1400
1200
1000
°C
2 Immiscible Liquids.
SiO2 and Liquid.
MnO and Liquid.
Teph + Liq
Rhod + Liq.
MnO and Tephroite.
Tephroite and Rhodonite.
Rhodonite and SiO2.
10
20
30
40
50
60
70
80
90
100
MnO
Tephroite
Rhodonite
SiO2
WEIGHT PER CENT OF SiO2.

Results of Optical Examination for the Identification of Phases.

The results of this examination may be stated very briefly. With 100% MnO only one phase is present with a refractive index between 2.10 and 2.20. It is deep green in colour and anisotropic. In the presence of SiO_2 MnO persists as a phase till the SiO_2 content reaches approximately 30% when it disappears. Between 0 and 30% SiO_2 a practically colourless phase is associated with the MnO. It has a refractive index lying between 1.78 and 2.00 and is apparently tephroite. Above 30% of SiO_2 a brown material occurs along with tephroite. Its refractive index lies between 1.76 and 1.78, which identifies it as rhodonite. Over approximately 46% of SiO_2 tephroite disappears and rhodonite is associated with tridymite of refractive index just under 1.55.

Two of the crucibles which cracked while the melts were being drilled out were sectioned, and the melts examined by reflected light. Of these one contained ~~of~~ 97% of SiO_2 and consisted of a white groundmass of silica, in which were embedded small globules of the red rhodonite phase. These appeared to have been entrapped by the freezing silica while themselves in the molten state, indicating that in all probability two immiscible liquids. exist in this part of the diagram at high temperatures. The other melt thus examined contained 50% of SiO_2 and was found to consist of a closely interwoven mixture of rhodonite and silica.

The Thermal Equilibrium Diagram of the System MnO-SiO_2.

The thermal equilibrium diagram of the system MnO-SiO_2, based on the data detailed above, is given in Fig. 25. Two compounds tephroite ($2MnO.SiO_2$), and rhodonite ($MnO.SiO_2$) occur. The only other phases are free MnO and SiO_2, and solubilities in the solid state, if they exist, are negligibly small. The transition temperatures given are based almost solely on the heating curves of the various mixtures, as the points on cooling were always subject to a considerable and very variable amount of supercooling.

On this basis the eutectic temperature is 1208-1210°C, as against 1195°C given by Doerinckel[1], whose diagram was based solely on cooling curves. The eutectic arrest, as can be seen from an examination of the curves reproduced, is however liable to show supercooling even when slow rates of cooling are employed, and it is quite to be expected that his results would be somewhat low. Determination of the eutectic composition in these viscous silicate melts is a matter of some difficulty as there is a tendency for a form of segregation to occur as already mentioned, and the normal fine-grained eutectic structures are not obtained. Doerinckel fixed the eutectic at 41% of Silica, but in the light of the present results 38% of Silica and 62% of MnO is a more probable composition. Herty[2] on the other hand observed by optical means that the eutectic melted at 1225°C, but the uncertainty of this method when unconfirmed by other means has already been pointed out. He considers 31% of Silica as the most probable composition of the eutectic.

Both of these workers agree with the present findings that two compounds occur, tephroite, the orthosilicate ($2MnO.SiO_2$), and rhodonite, the metasilicate ($MnO.SiO_2$), and further that these compounds undergo peritectic dissociation on melting. Fig. 25 gives 1330°C as the temperature of the tephroite peritectic. This figure is identical with that quoted by Doerinckel. In the case of melts in this region of the diagram much less supercooling was, in general, observed, which probably explains the close agreement with regard to this temperature. Herty's figure of 1375°C is certainly too high. The temperature of the rhodonite peritectic dissociation is now given as 1275°C. This point invariably showed considerable supercooling and the value 1220°C would again be low. Herty gives 1280°C for this reaction.

With regard to the position of the liquidus lines the present work differs somewhat from the earlier determinations. For one thing the melting point of MnO is undoubtedly much higher than previously supposed, and the slope of the liquidus on the left of the diagram is accordingly steeper. Further the slope of the liquidus on the Silica side of the eutectic is very steep

and even at the rhodonite composition a temperature of 1430°C is required to give complete fusion. For Silica contents in excess of 50% the position of the liquidus was rather difficult to determine as the thermal changes obtained were very sluggish and ill-defined. Certain of these melts were found to contain rounded globules of rhodonite in a groundmass of pure white silica indicating immiscibility in the liquid state. This part of the diagram has therefore been drawn in somewhat qualitatively as shown, and agrees reasonably closely with that suggested by Greig[3].

No solubility ranges have been indicated, as, if these occur, they are certainly very minute, and the refractive indices obtained appear to be those of the pure materials.

Table of References Given in Part One; Section 1.

1 .F. Doerinckel : Metallurgie VIII, 1911, P281.

2. C.M.Herty; Metals and Alloys, I, No. 18, 1930, P883.

3. J.W.Greig; Am. Journal of Science, XIII,2, 1927, P133.

4. - Glaser; see Herty above.

5. - Cain; See Herty above.

6. J.H.Andrew, W.R.Maddocks, and D.D.Howat; Journal of the Inst. of Iron and Steel, 1931, No.2, P283.

7.- Merwin and - Larsen; Am. Journal of Science, 34, 1912, P42.

8. - Birnbauer and - Tude; J.W.Mellor's Treatise on Inorganic Chemistry, Section on MnO.

9. C.Benedicks and H.Löfquist; "Non Metallic Inclusions in Iron and Steel" Chapman and Hall (1930), P72.

PART I - SECTION 2.

THE THERMAL EQUILIBRIUM DIAGRAM OF THE BINARY SYSTEM FeO-MnO.

Experimental procedure: The system FeO-MnO was investigated by the method developed for the system $MnO-SiO_2$, the furnace employed being the same, and the arrangement of crucible, blank, thermocouples, etc. identical with that already described.

One modification had, however, to be introduced owing to the ease with which FeO is reduced to iron, or oxidised to higher oxides. It was necessary to carry out all work on these melts in vacuo, or, failing that, in an inert atmosphere. For this purpose a "Pythagoras" tube of 2 inches internal diameter was inserted inside the furnace tube as shown in Fig. 26. (See also Andrew, Maddocks, and Howat[1]). The molybdenum grid was then bound direct to the Pythagoras tube and the inner alundum sleeve (see Fig. 1) dispensed with. The cylindrical container for the melt and blank was placed inside the "Pythagoras" tube, which was closed at the top end by a three-holed rubber bung. Through the holes in this bung were inserted short lengths of glass tubing, one of which was connected by rubber pressure tubing to a mercury pressure gauge and "Cenco Hyvac" vacuum pump. The other two provided egress for the thermocouple leads. They were sealed after the leads had been threaded through them by tightening screw clips on the short pieces of rubber tubing attached to them. All joints and connections were painted with a solution of celluloid in amyl acetate to render them vacuum tight. For the more fusible melts, when temperatures in excess of 1450°C were not required, melting was carried out in vacuo. At higher temperatures there was a danger of the "Pythagoras" tubes collapsing, so nitrogen was introduced, the pressure being so arranged that, at high temperatures, it reached a value of just over one atmosphere.

Apart from this the technique was the same, the differential method being employed throughout.

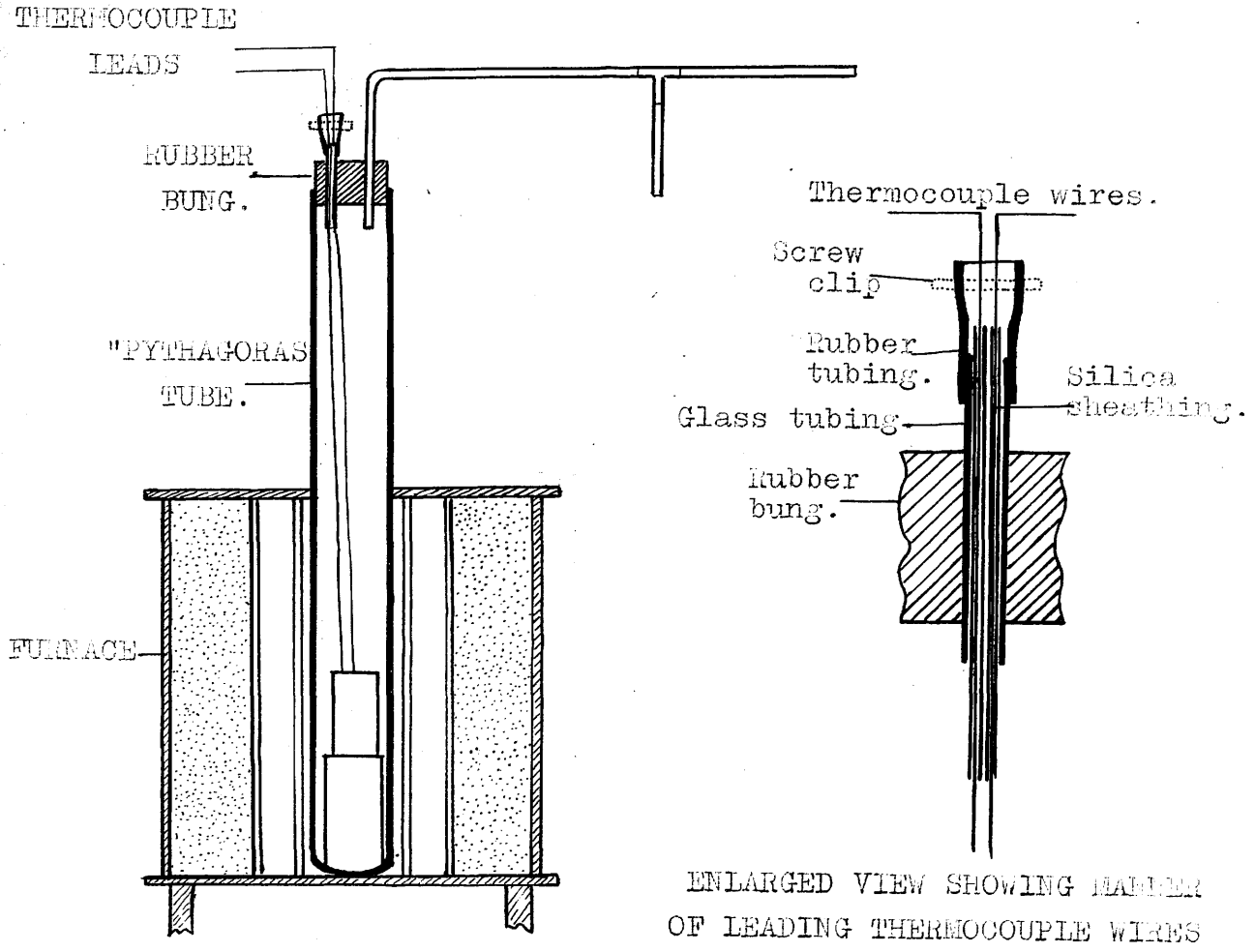


FIG. 26. DIAGRAM OF APPARATUS EMPLOYED FOR MELTING IN VACUO.

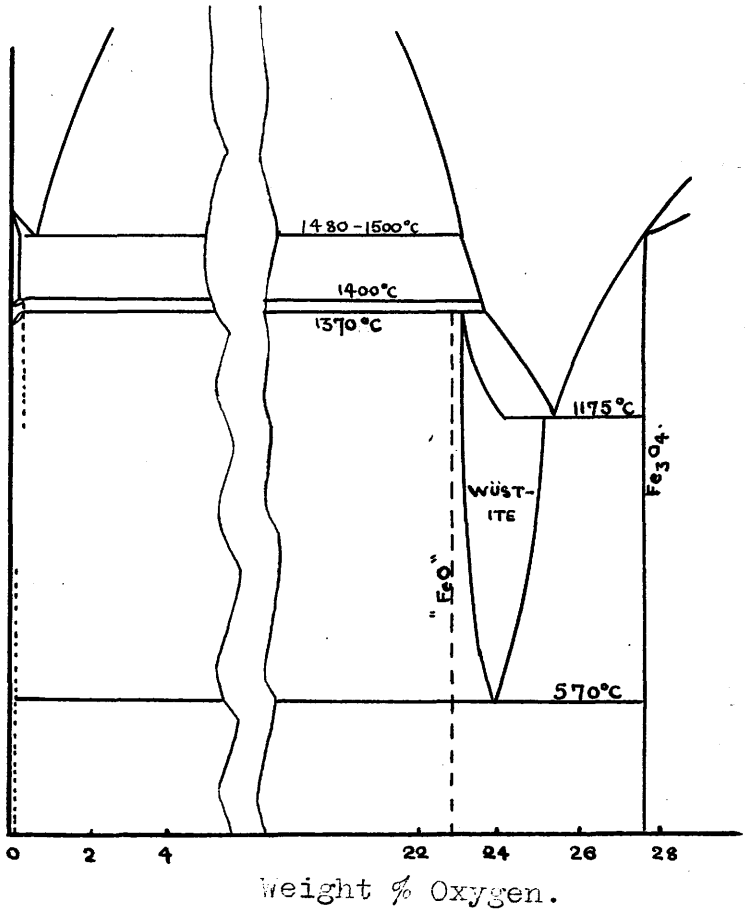


FIG. 27. PART OF THE IRON-OXYGEN DIAGRAM ACCORDING TO MATHEWSON, SPIRE AND MILLIGAN.

Preparation of Materials.

Preparation of MnO: This was carried out as described in Part 1, Section 1.

Preparation of FeO: FeO was prepared according to the method given by Andrew and co-workers[1]. In the present instance decomposition in vacuo at 600°C was followed by roasting a short time at 1000°C. The product was tested by analysis for total iron (though the limitations of this method are realised), and by the magnet for presence of Fe_3O_4. It was difficult to obtain the material in the absolutely non-magnetic form, presumably because of the instability of FeO at all temperatures under 575°C (see below). Further if the initial heating to 1000°C were omitted, the product was liable to become magnetic in air due to spontaneous oxidation, and it was, in extreme cases, actually pyrophoric in nature.

The substance so prepared was a black or blue-black powder. When prepared under the most favourable circumstances, its magnetism was so slight as to be barely detectable, but was probably never completely absent. Analysis for total iron showed the iron content to approximate very closely to 77.5% (theoretical FeO, 77.78%), though in the case of the more magnetic batches it was slightly lower than this.

Note on FeO: The material ferrous oxide, it is now fairly well established, is unstable at all temperatures under 575°C, where it undergoes a dissociation into Fe_3O_4 and free iron containing a certain amount of oxygen solution. It can, however, exist at room temperatures in the metastable condition, owing to the fact that the conversion is slow even at temperatures just under 575°C. (See Benedicks and Löfquist[2].) At 1370°C on the other hand, it melts incongruently to give an oxygen-rich liquid and a solid iron-rich phase which does not dissolve completely till considerable higher temperatures are reached. Any binary system of the type FeO-MnO or FeO-SiO_2 of which FeO forms one of the constituents cannot, therefore, be regarded

as a true binary system as the dissociation of FeO results in the formation of phases whose composition cannot be expressed on the diagram. As an approximation, however, this is usually neglected, as it is probable that in most systems its effect will be slight, and, moreover, will be confined to a short range of composition at the FeO end of the diagram.

Again between 575°C and 1370°C so-called ferrous oxide has a considerable range of existence as regards composition, and it can dissolve appreciable amounts of iron on the one hand, and oxygen (or Fe_3O_4) on the other. The name Wüstite has been applied to the material existing over this range. There is, moreover, considerable evidence in existence which indicates that this range does not include within its boundaries the chemical composition FeO, and that Wüstite always contains an excess of oxygen over that required by the formula. This has been verified by thermal and chemical data[3], by X-ray measurement of the Wüstite lattice[4], and by measuring the amounts of CO and CO_2 at equilibrium with a solid phase containing varying amounts of oxygen at temperatures in the region of 900°C[5]. On the other hand several workers have reported the preparation of oxide analyzing practically 100% FeO, which should be impossible if the above view is correct, and at the present moment the weight of evidence in its favour seems to suggest that it is. The Wüstite region of the iron-oxygen diagram as proposed by Mathewson, Spire and Milligan[3] is reproduced in Fig. 27.

Experimental Results.

Heating and Cooling Curves: A selection of the heating and cooling curves obtained is the accompanying diagrams.

Curves for FeO: In view of the peculiarities of Ferrous Oxide described above, and also because of the difficulties involved in its accurate analysis (a very small weight of oxygen in FeO can represent a very considerable proportion of Fe_3O_4), a considerable number of heating and cooling curves were carried

out with a view to determining the possibility of error from this source.

First of all a series of curves was taken with a sample of "non-magnetic" FeO (Fig. 28). There is an indication of a slight arrest at 1160-1170°C which is rather more pronounced on the first heat than on the second. This apparently corresponds to the eutectic between FeO and Fe_3O_4, and it is quite characteristic of such points that it is larger on the first heat when the material was in all probability not perfectly homogeneous. The bulk of the material appears to melt at 1370°C on the first heat, and at a slightly lower temperature -1355°C- on the second. This might be caused by the improved heat conductivity of the crystalline as opposed to the initial powdered material, or, alternatively, by the more uniform distribution of the Fe_3O_4 content. If any very considerable increase of the total Fe_3O_4 content had taken place, for example due to an insufficient degree of vacuum, the eutectic point might have been expected to show an increase instead of a diminution in size. There is a slight indication of a point at 1410°C, corresponding possibly with the A_4 point in the free iron liberated at the peritectic. Finally melting is completed at 1480°C. The cooling curves show evidence of all these points somewhat supercooled.

Owing to the slight discrepancy between the temperatures 1370 and 1355°C obtained for the peritectic reaction on the first and second heatings respectively, it was thought desirable to repeat a similar series of determinations a large number of times on a given sample to see if this change was progressive. The particular sample was melted no fewer than six times. The initial depression took place as before but after the first heat all subsequent curves were practically identical in contour. To apply a still further check a series of melts was carried out in platinum. The results again agreed very closely, although it was evident on removal from the furnace that the platinum had dissolved an appreciable amount of iron. No visible trace

of reaction could ever be found with molybdenum though test crucibles were sectioned and examined microscopically, the only exception to this being provided by one case when the "Pythagoras" tube cracked and allowed hydrogen to pass inside. The free iron formed by reduction alloyed with the crucible causing pitting of the surface, and the formation of an iron-molybdenum alloy was easily detected under the microscope.

Still another sample of FeO was investigated (Fig. 29) to find whether even the most magnetic batches would cause serious discrepancies. For this purpose a fraction was separated from some of the more magnetic material by means of a magnet. The general form of the curves is similar but the 1170°C point is more pronounced, as is the continuous range between this point and the peritectic or temperature of maximum melting, which is further lowered by about 10°C. This was, of course, an extreme example, and it is therefore fairly certain that with the precautions taken to keep the magnetic content of the oxide to a minimum no serious discrepancies would arise from this source. In practice all samples which were at all strongly magnetic were rejected.

It is of considerable interest to compare these iron oxide curves with the diagram of Mathewson, Spire, and Milligan given in Fig. 27. The temperatures of the arrests agree very closely with the temperatures given on the diagram. The fact that the eutectic arrest occurs with melts so high in iron and in association with the peritectic, would suggest, however, that the boundary of the Wüstite range should be displaced somewhat on the oxygen-rich side to somewhat lower oxygen concentration.

Curves of FeO-MnO Mixtures: In interpreting the curves for the system FeO-MnO a slightly different procedure was adopted than in the case of the MnO-SiO_2 melts. There were indications that a solid solution melting range tended to give an elongated but continuous deviation of the differential galvanometer. The termination of these ranges has, therefore, been taken in

"FeO".

(Nonmagnetic).

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

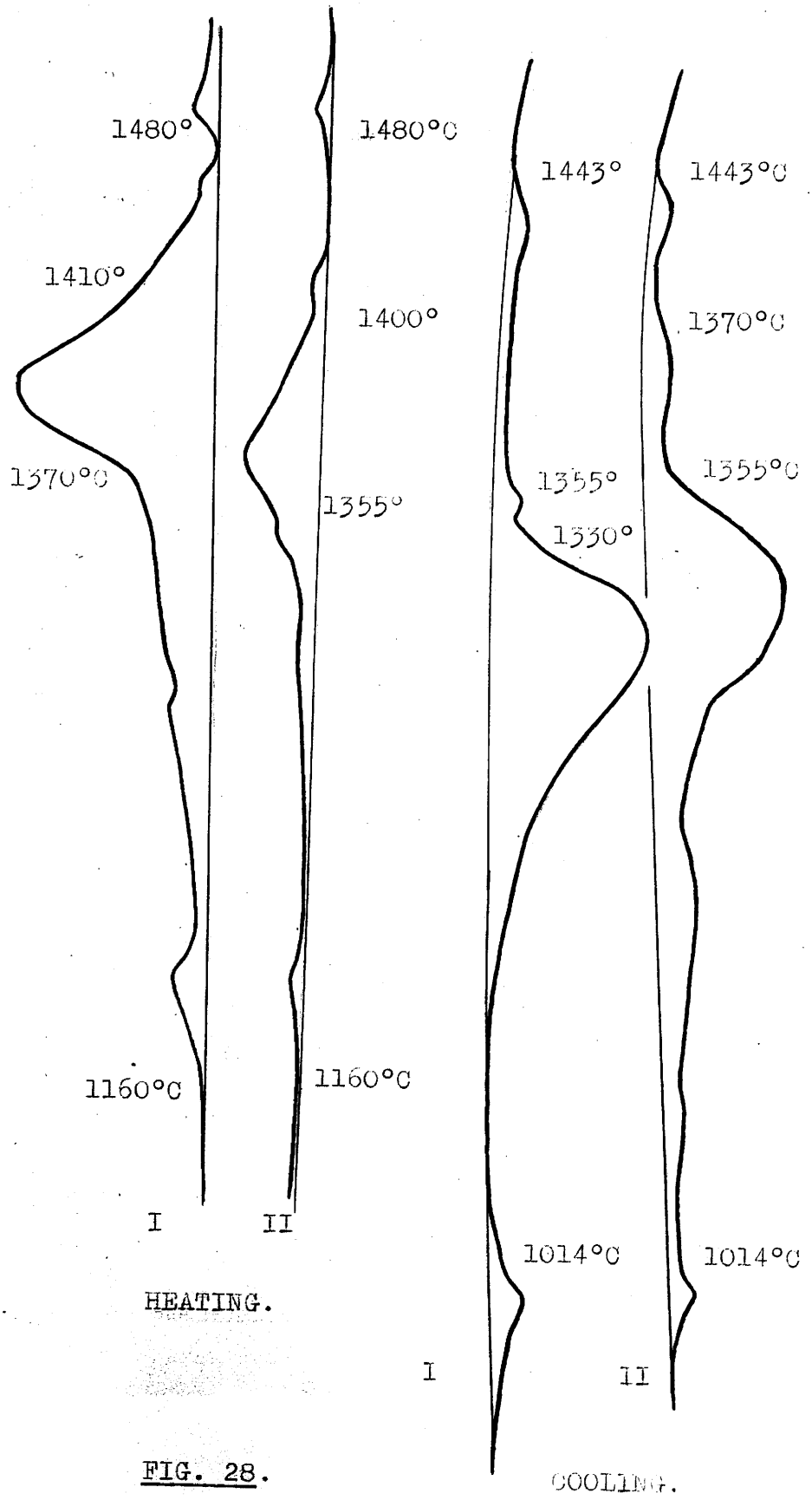


FIG. 28.

"FeO" selected from a magnetic batch with a magnet.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

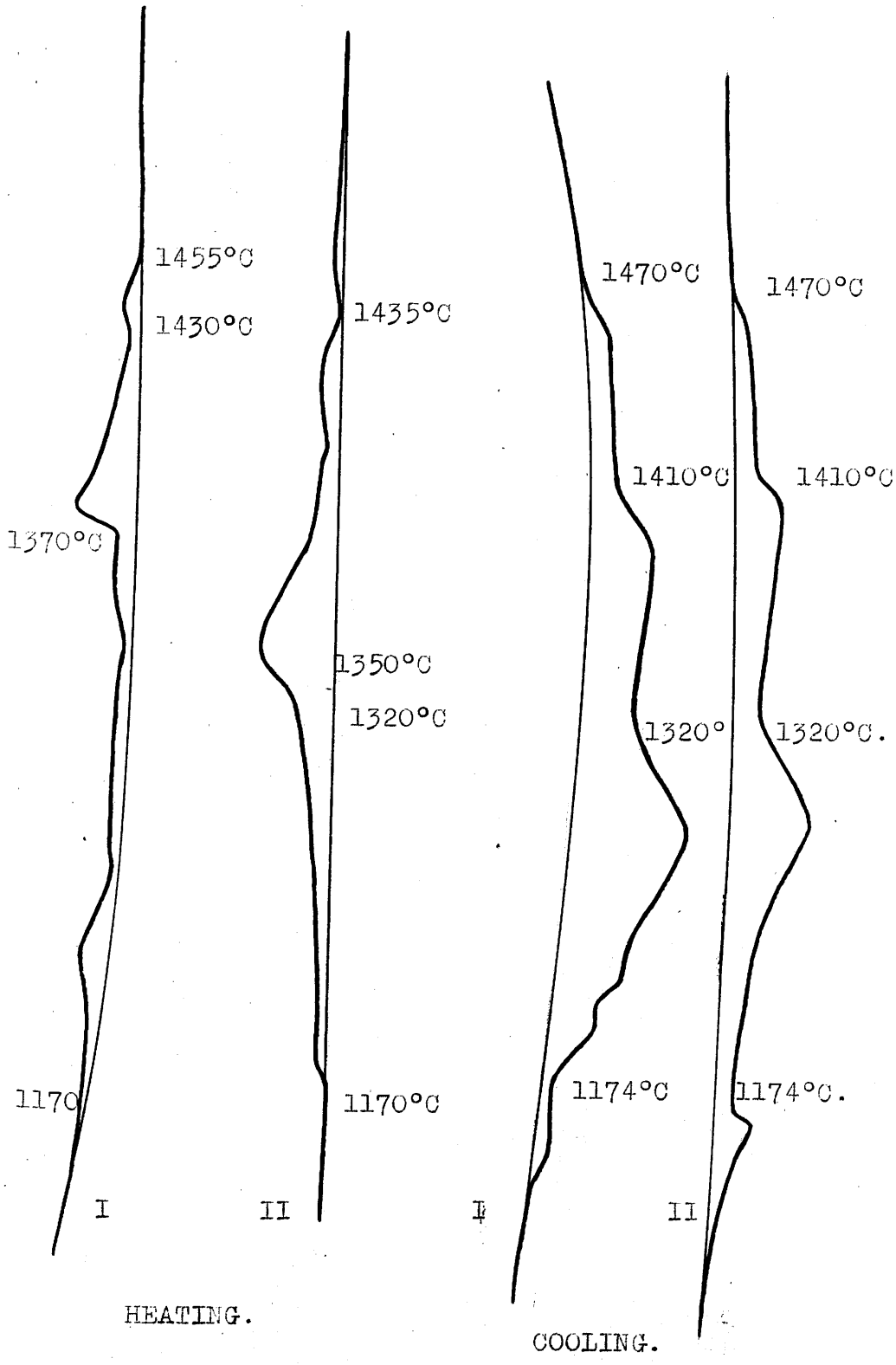


FIG. 29.

MnO : 10.
FeO : 90.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

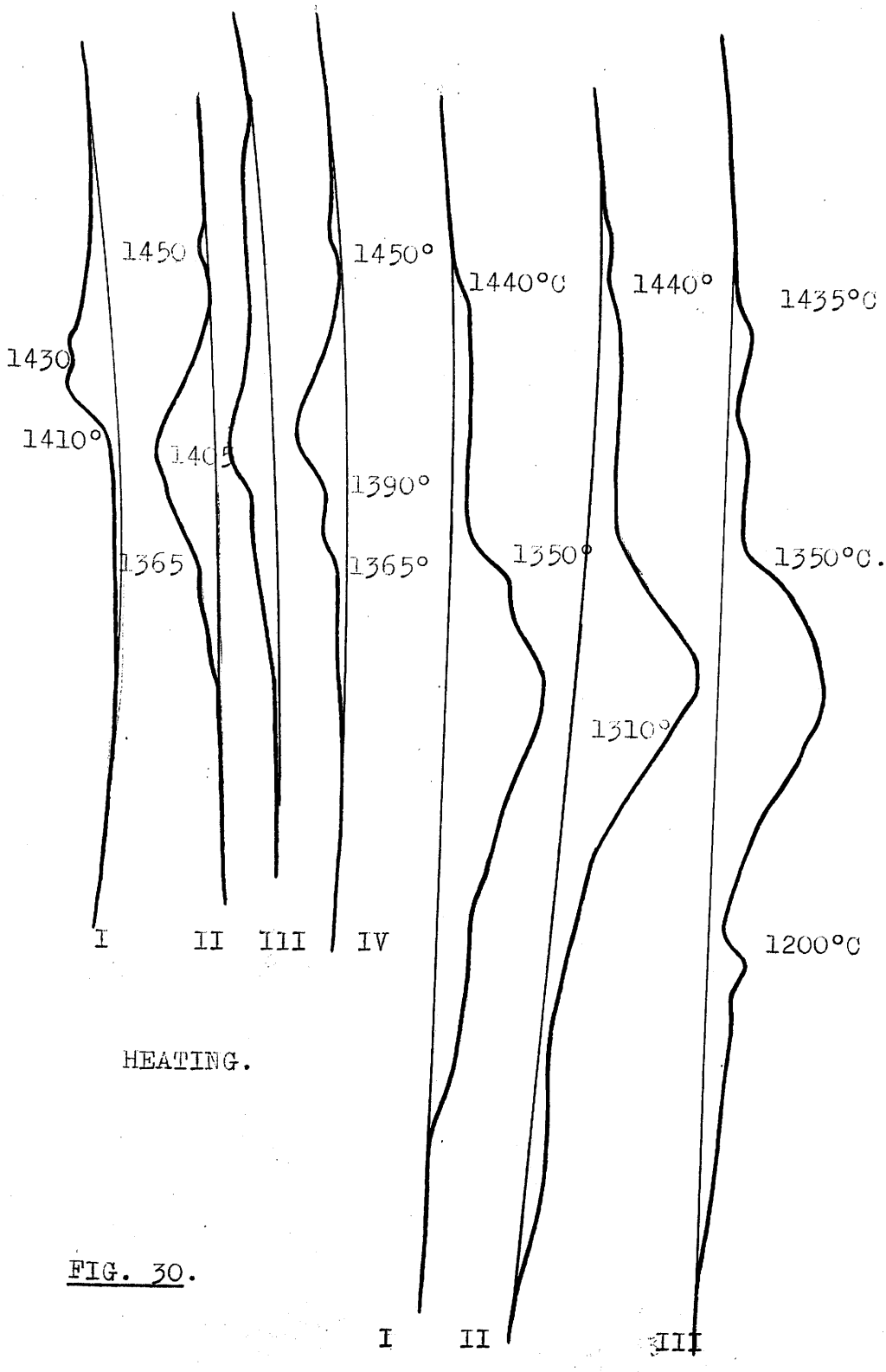


FIG. 30.

MnO ; 20.

FeO : 80.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

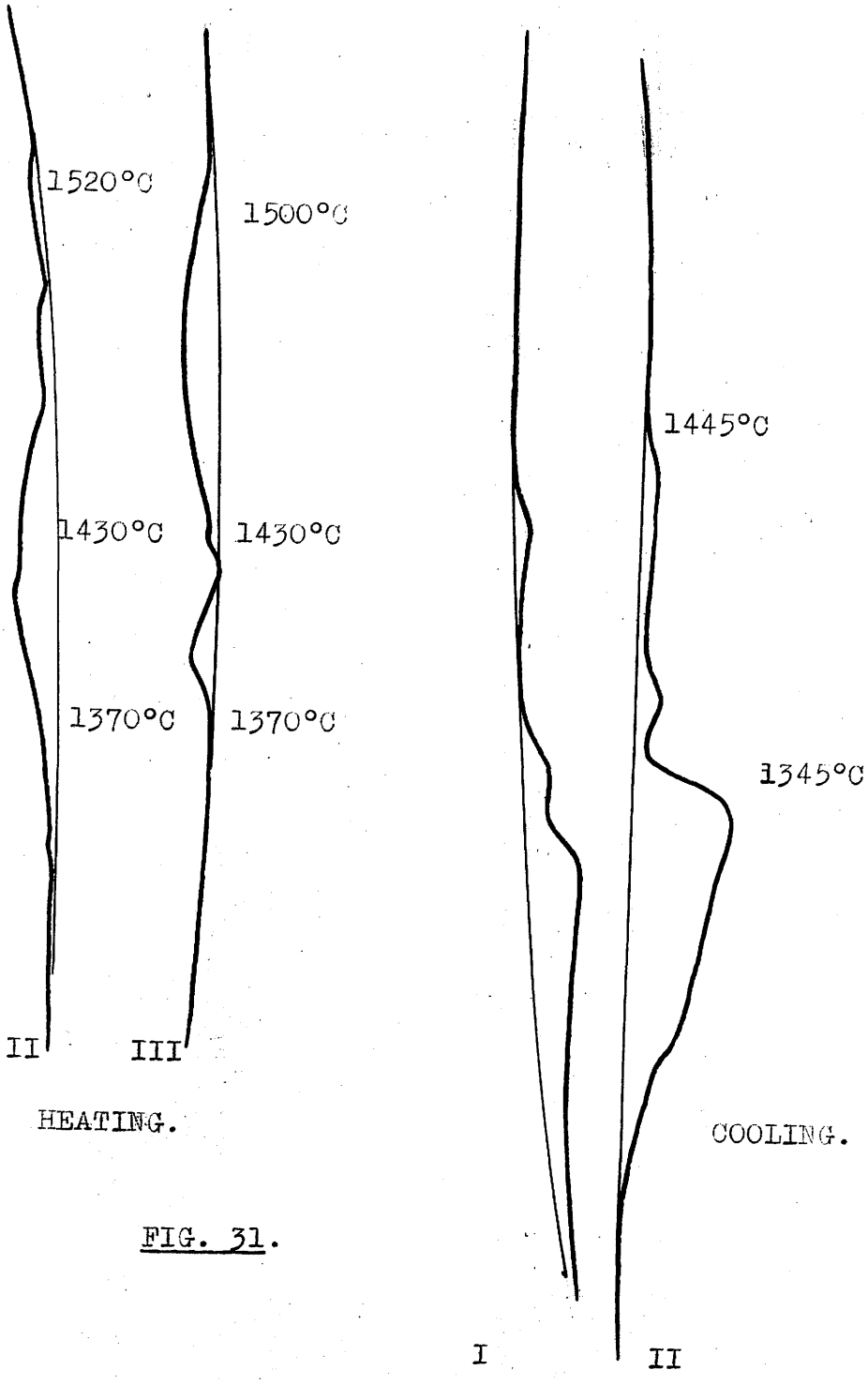


FIG. 31.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

MnO : 30
FeO : 70.

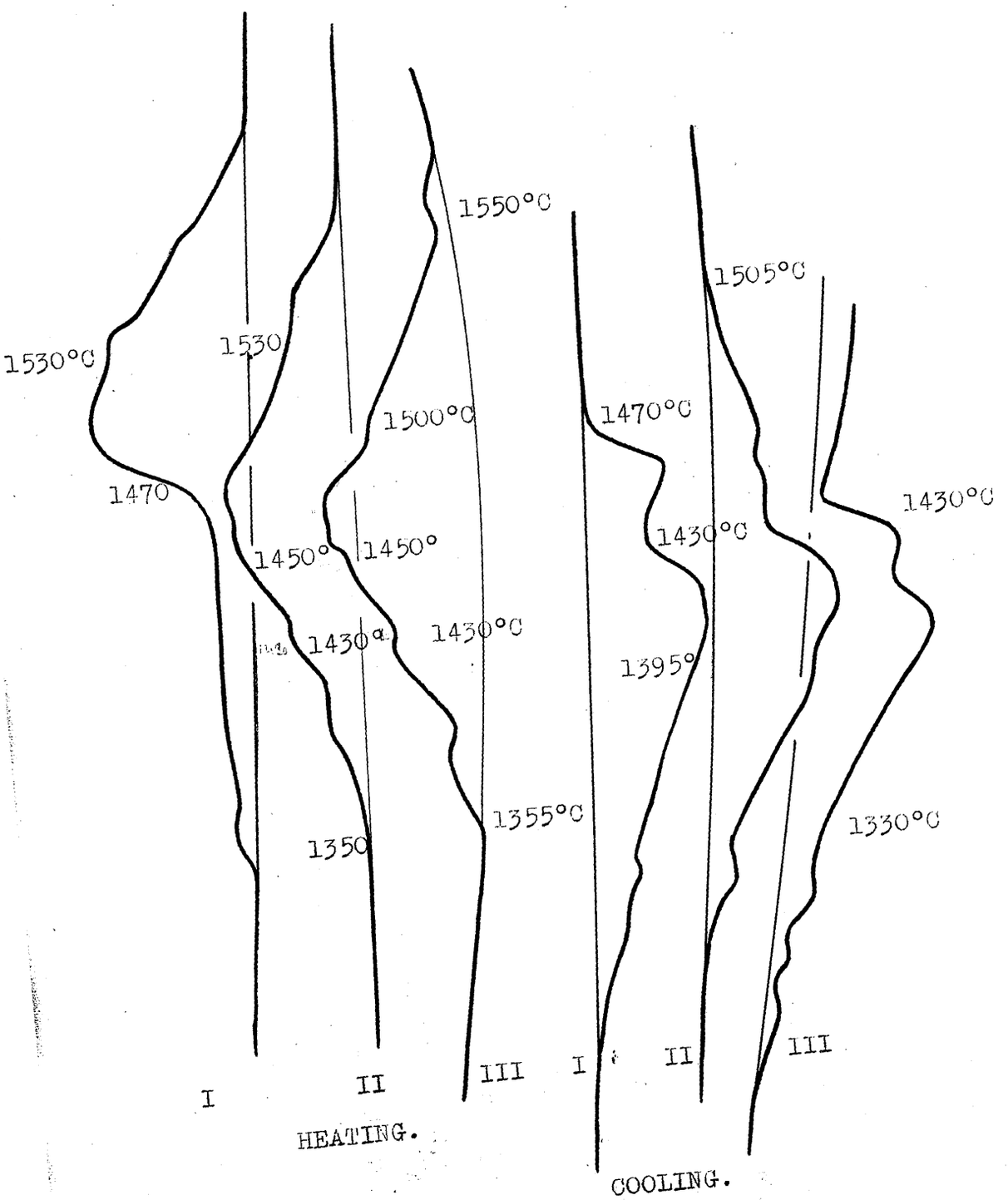


FIG. 32.

MnO : 40.
FeO : 60.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

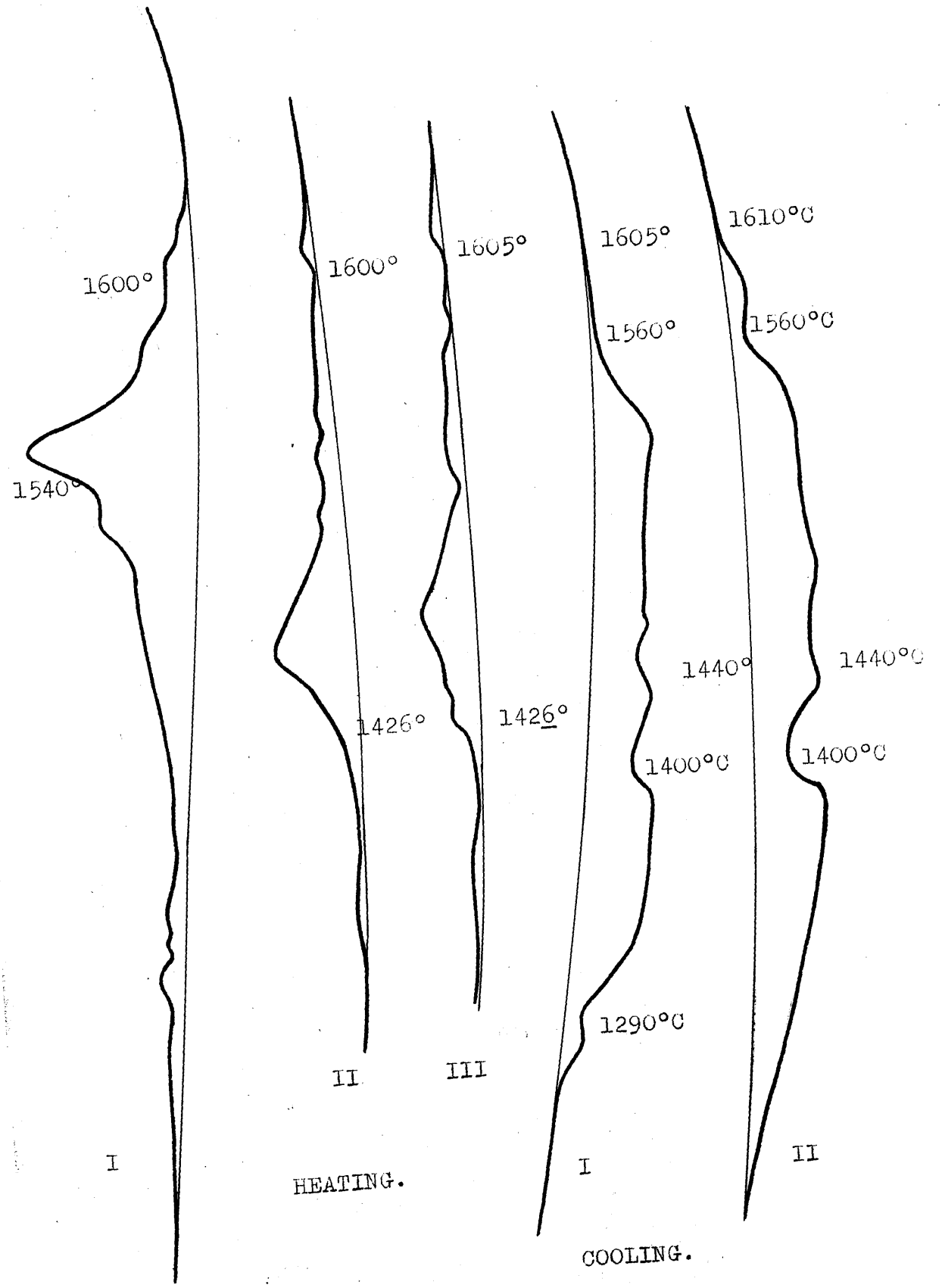


FIG. 33.

MnO : 50.
FeO : 50.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

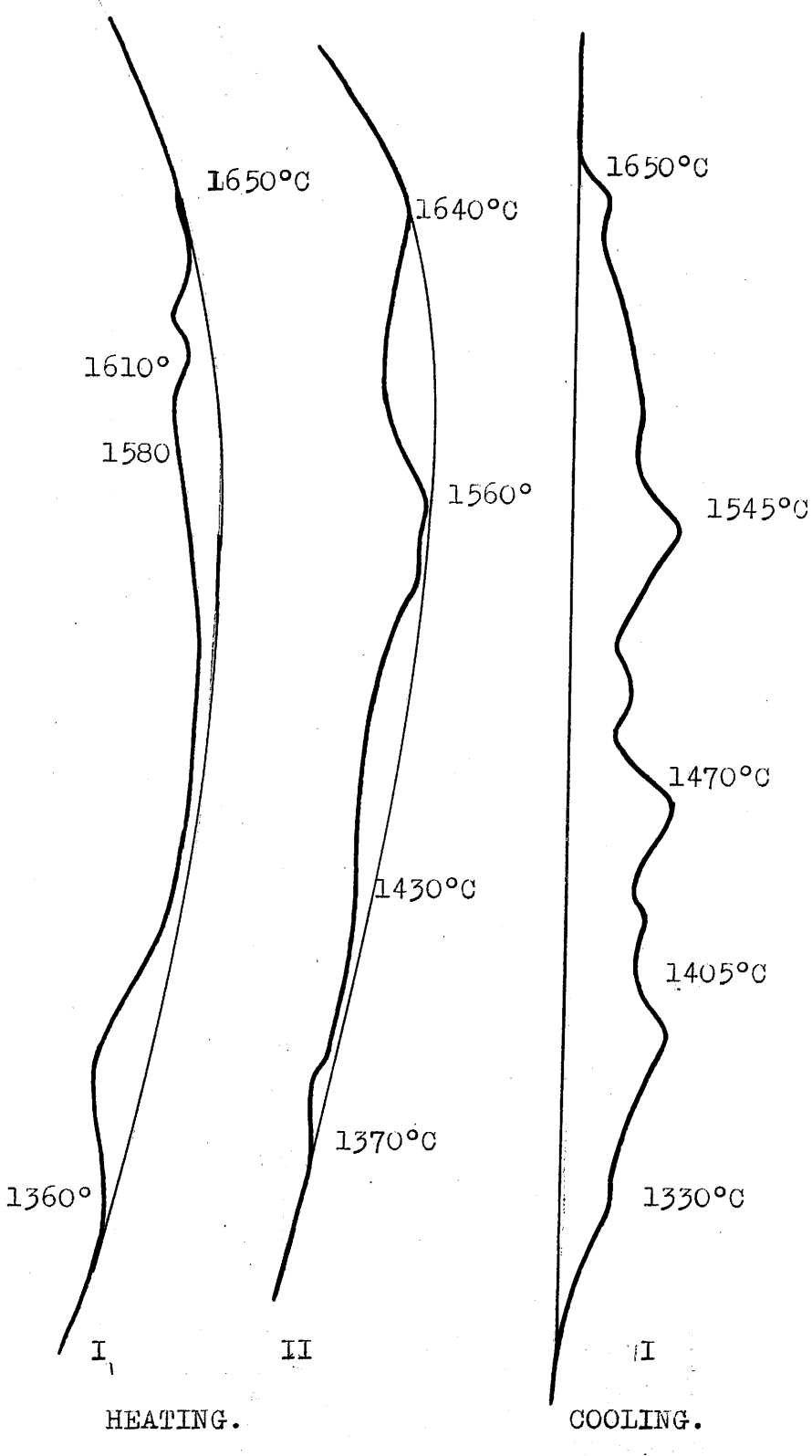


FIG. 34.

MnO : 60.

FeO : 40.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

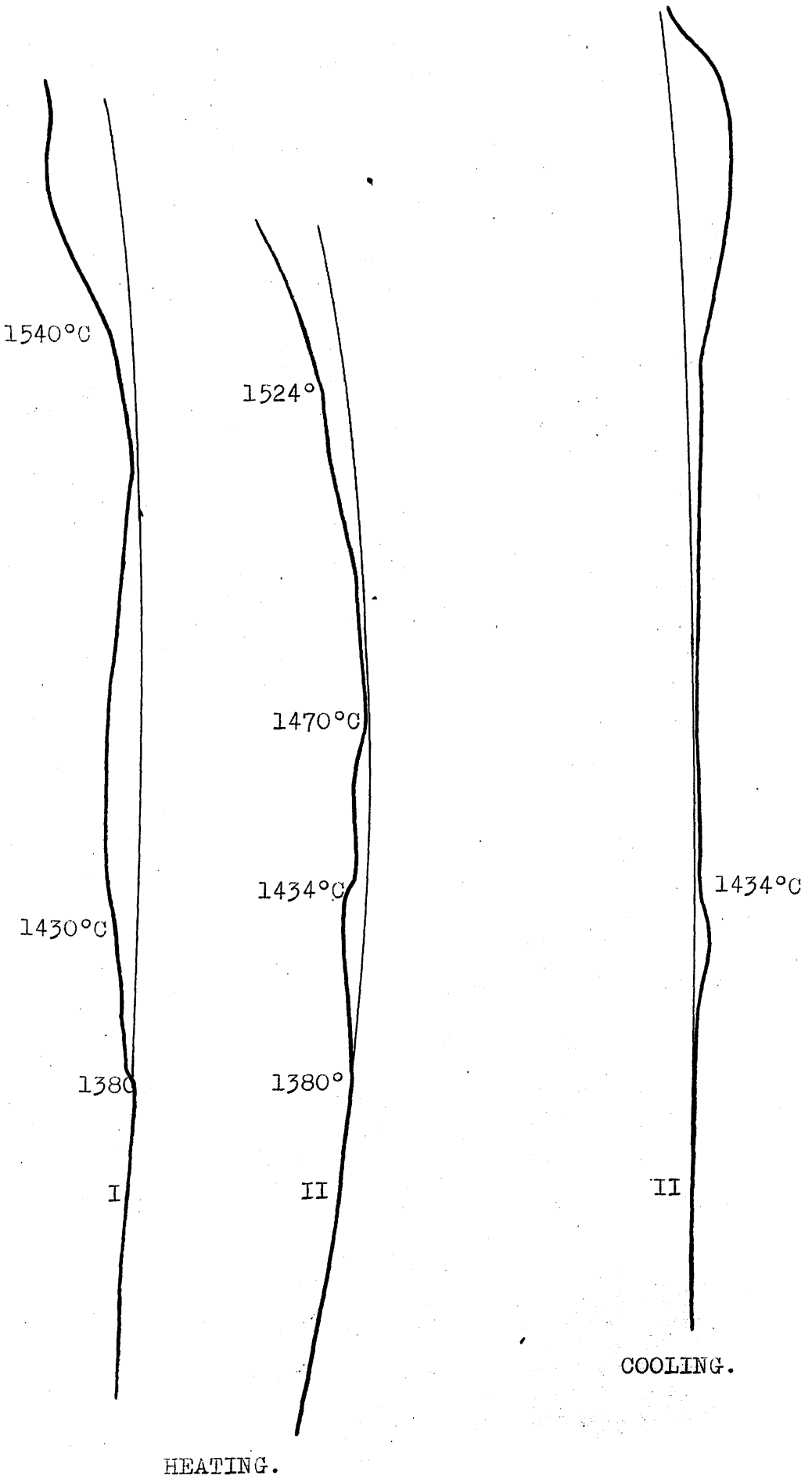


FIG. 35.

most cases to indicate the position of the liquidus. Whenever possible (when it was obvious that supercooling had not occurred) this was verified by noting the point at which freezing began on the corresponding cooling curves.

With 90% FeO the liquidus is placed at 1410°C the solidus at 1365°C. A slight bulge higher than this is probably given by traces of the iron rich phase mentioned earlier. The cooling curves also show this deviation corresponding very closely with a similar one on the cooling curves of FeO itself.

With 80% FeO there is a break in the range and it is probable that the peritectic reaction at 1430°C takes place in this melt.

With 70% FeO there are indications of four distinct bulges. The bottom one may indicate the position of the solubility curve in the solid state, but this is of course uncertain and must be regarded as hypothetical. The arrest at 1430°C is now much larger. As the content of MnO is increased the melting range becomes increasingly prolonged but there is always an indication of an invariant point at 1430°C. Determination of the liquidus at the high MnO end of the diagram presents practically insurmountable difficulties owing to the necessity of maintaining an inert atmosphere, and the fusibility of Pythagoras tubes at temperatures in excess of 1650°C. With the melting point of MnO known, however, and the type of diagram involved, its course can be predicted with a considerable degree of probability. A number of incomplete curves were carried out in this region to explore the solidus, the mixtures being first subjected to a prolonged soaking at the highest attainable temperature in an endeavour to ensure equilibrium.

The Thermal Diagram of the System FeO-MnO.

Several different forms of this diagram have been proposed. Andrew and coworkers[1] give an unbroken series of solid solutions, with melting points ranging from 1410°C, the proposed melting point of FeO, to 1585°C, the proposed melting point of MnO. In this diagram the temperature range between liquidus and

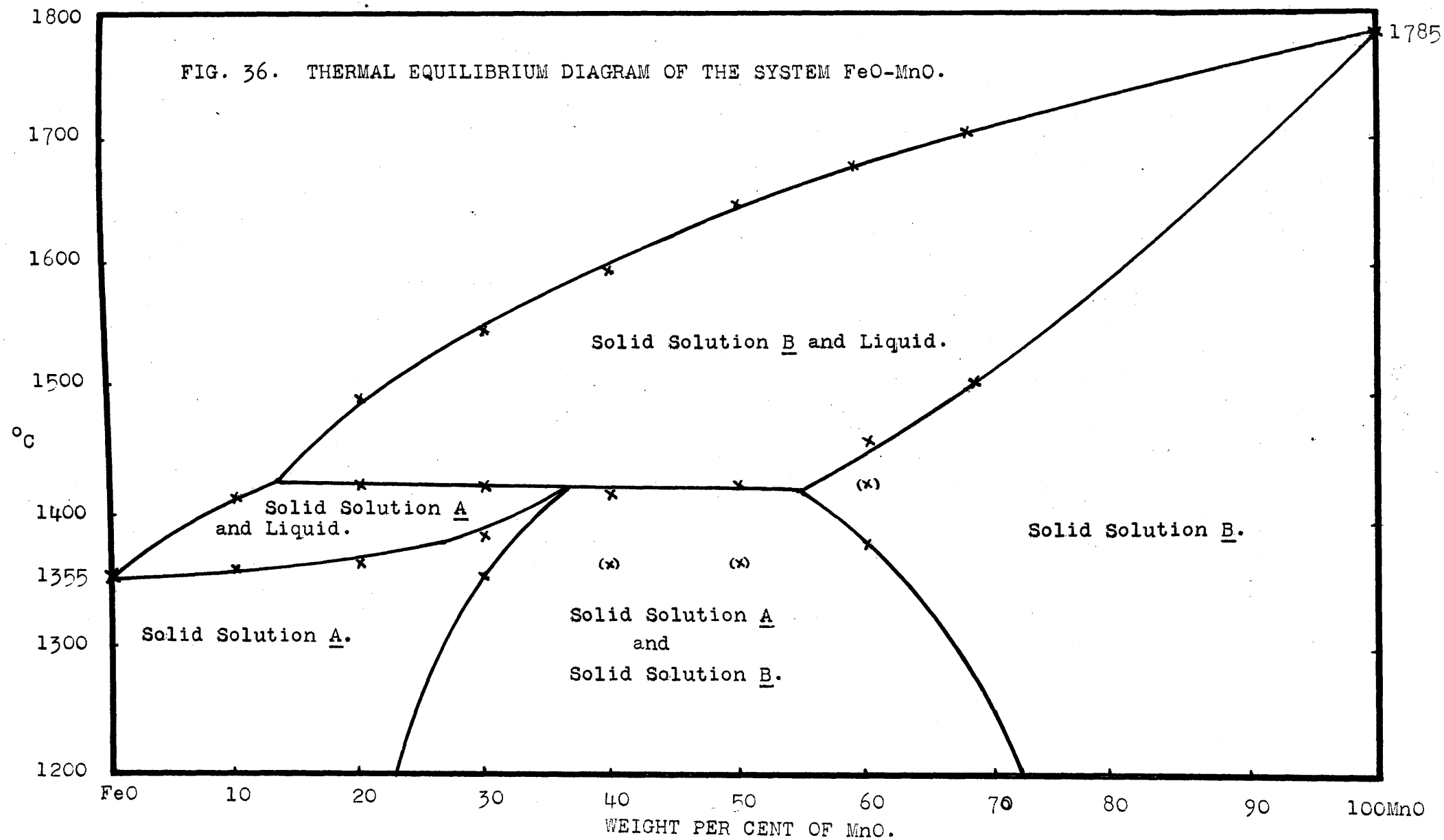


FIG. 36. THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM FeO-MnO.

solidus is very small. Herty[6] gives a similar type of diagram, with melting points ranging from 1370°C (FeO) to 1610°C (MnO). It differs from Andrew's in that the liquidus and solidus are separated by an exceedingly wide temperature interval, which would indicate that the two oxides just fail to show immiscibility.

Benedicks and Löfquist[7] give a diagram of the type now advanced, showing only partial miscibility in the solid state. The available evidence, including thermal data and the results of microscopic examination of fused mixtures of FeO and MnO, is surveyed by these authors who come to the conclusion that this is the most probable type of diagram.

It is difficult to explain the invariant point at 1430°C on any other assumption than that a peritectic reaction between two phases occurs. It may be mentioned that a diagram of this type would appear to fit the points got by Herty almost as closely as the one he favours.

Optical Examination of the Melts.

The method adopted for the identification of phases was the same as that described in Section 1. Owing to the high refractive indices of the materials glasses of sulphur and selenium had to be employed throughout. The opaque nature of the materials rendered the application of the method rather more difficult than usual, but it was found that light could be got through the very thinnest portions of the powder fragments to a sufficient extent to enable measurements to be made.

The refractive index of FeO itself was found to have the value 2.0. With addition of MnO up to the limit of solubility it increases up to a limiting value of approximately 2.10. Simultaneously a new phase with a characteristic greenish colour appears with a refractive index, as near as can be estimated, of 2.13 but increasing with increasing MnO to 2.16 the value for pure MnO.

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3. Mathewson, Spire and Milligan, Trans. of the American Society for Steel Treatment, 19,No.1, 1931.
4. E.R.Jette and F.Foote, Am. Inst. of Mining and Met. Engineers, Iron and Steel Division, Contrib. No. 7, Class C, 1933.
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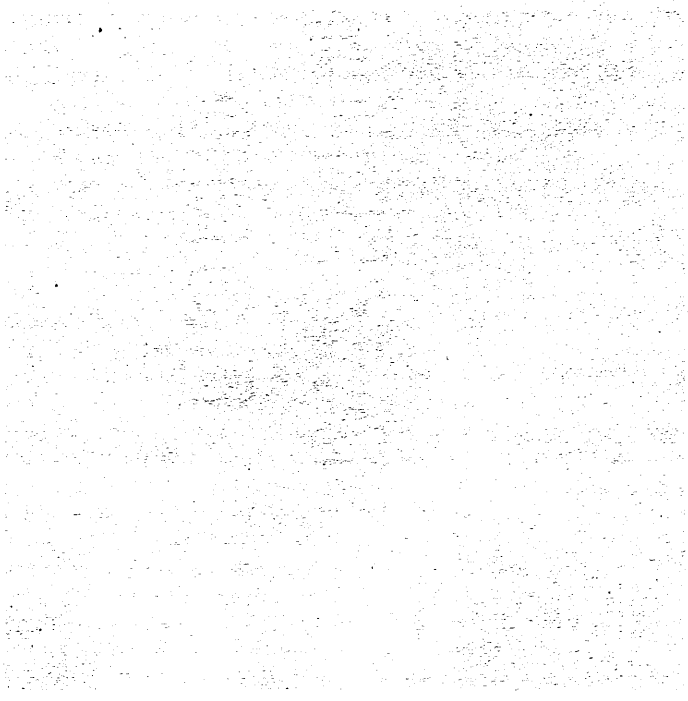
7. C.Benedicks and H.Löfquist, ibid, P74.



PART 1 - SECTION 3.

THE THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM $FeO-SiO_2$.

The binary system $FeO-SiO_2$ is one of considerable importance in the fields of general ceramics, petrology, and both ferrous and non-ferrous metallurgy. It has accordingly been investigated by various workers and a number of diagrams have been proposed which, however, vary somewhat in their essential features. The chief difficulties encountered are, as in the case of the $MnO-SiO_2$, the high temperatures involved and the very corrosive nature of the melts, which makes it extremely difficult to find crucibles which will enable melting to be carried out without serious contamination taking place.

The main points on which the various suggested diagrams differ are with regard to the exact fixing of the melting temperatures and also as to the compounds formed between the components. Two such have been propounded. Of these the orthosilicate, fayalite, ($2FeO.SiO_2$) can be considered definitely established. The metasilicate ($FeO.SiO_2$) is of uncertain existence and was included in the earlier diagrams mainly because a somewhat rare silicate, grünerite, of approximately this composition is found in nature. Of the several workers on this system von Keil and Damman[1] investigated mixtures with up to 40% of SiO_2 which range does not include the grünerite composition. Whitely and Hallimond[2] proposed a diagram which was mainly qualitative and was based on the microscopic examination of slags. They appear to favour the existence of grünerite. Greig[3] working on the high SiO_2 end of this diagram by means of quenching experiments found evidence of immiscibility in the liquid state between the compositions 60% and 97% of SiO_2. Benedicks and Löfquist[4] constructed a diagram based on the findings of von Keil and Damman and of Greig in which grünerite is tentatively included. Herty and Fitterer,[5] on the other hand, show only fayalite on their diagram. Bowen and Schairer[6] also support the contention that grünerite does not

exist. Their diagram was based on the examination of melts quenched from different temperatures in the manner of Greig. They were unable actually to melt the grünerite composition owing to its high melting point but they state that a melt which should theoretically have contained 80% of grünerite gave, when subjected to X-ray analysis, indications of the fayalite lattice only with a background of scattered radiation which they attribute to free SiO_2 in the glassy state.

In general configuration the several diagrams detailed above resemble each other to a certain extent and the results of the various researches can be summarized briefly. Between FeO and fayalite a eutectic exists the composition being given variously as 4% (K and D), 22% (H and F), and 24% SiO_2 (B and S) and the eutectic melting temperature as 1075°C (K and D), 1237°C (H and F), and 1177°C (B and S). A maximum in the liquidus is reached corresponding to the fayalite composition, the melting point of which is given as 1503°C (K and D), 1330°C (H and F), and 1205°C (B and S). Between fayalite and SiO_2 (or grünerite) is a second eutectic at 40% SiO_2 (K and D), 35% SiO_2 (H and F), or 38% SiO_2 (B and S), the temperature of melting being given as 1115°C (K and D), 1250°C (H and F), and 1178°C (B and S). On the SiO_2 of this eutectic the liquidus slopes somewhat steeply to the region of immiscibility described by Greig where melting takes place to give two liquids at an invariant temperature of 1698°C±15. If grünerite does exist it will in all probability melt incongruently in analogous fashion to $MnO.SiO_2$ and so the question of the existence or non-existence of this compound can have little effect on the contours of the liquidus.

In view of the success attained with the use of molybdenum as a refractory, it was considered highly desirable to work out this system by the methods already developed in an endeavour to remove some of the uncertainties just described.

Preparation of Materials.

The melts were made up by mixing the appropriate amounts of FeO and SiO_2. These materials were prepared as already described.

Experimental Procedure.

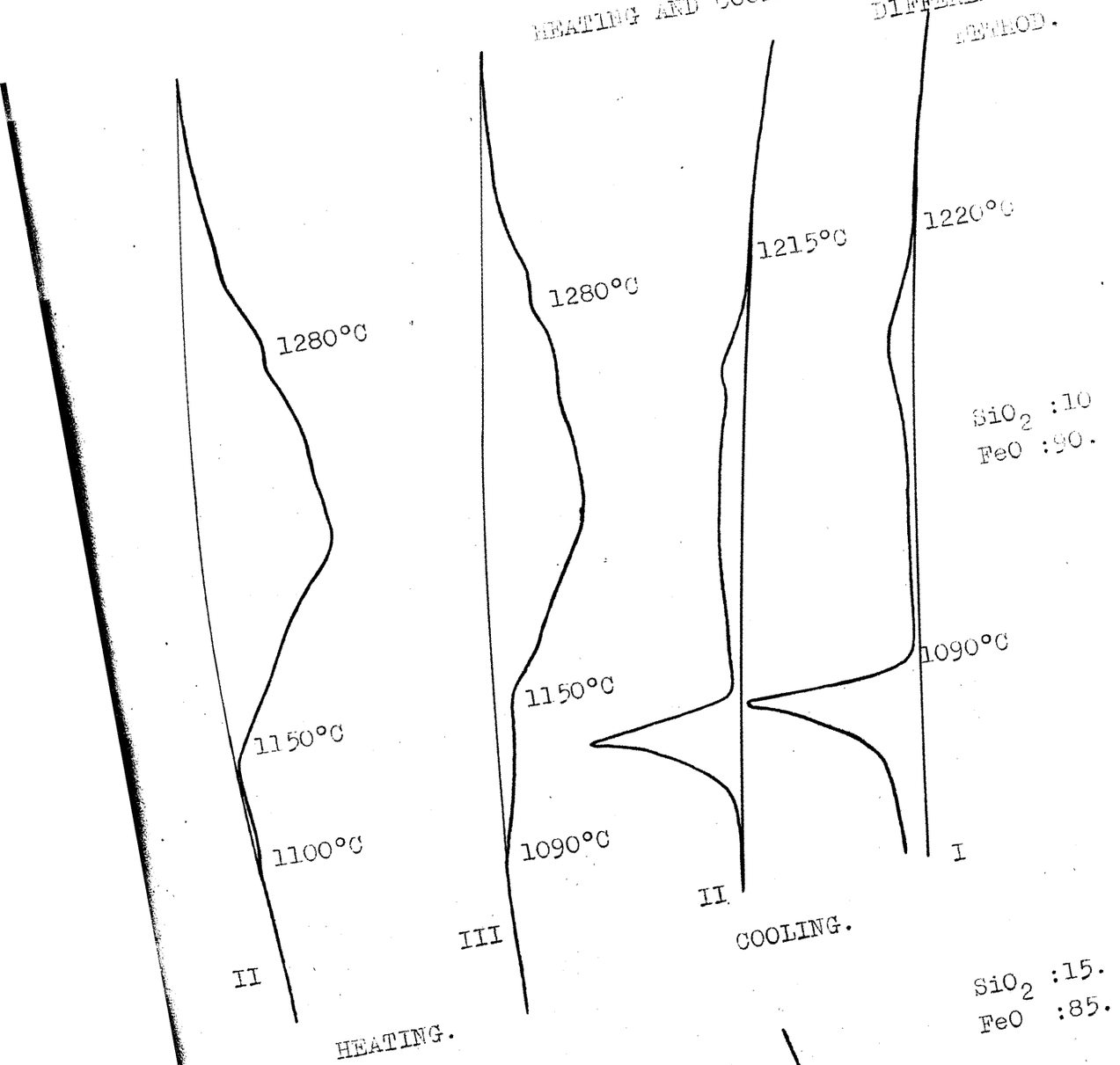
The apparatus employed and the technique were exactly as described for the investigation of the system FeO-MnO, heating being carried out in vacuo, or in the case of the more refractory melts, in an atmosphere of nitrogen to prevent collapse of the "Pythagoras" tubes. It was noticed that for some reason as yet unexplained nitrogen had a deleterious effect on the performance of the thermocouples and curves obtained with this gas in the tube were always much more irregular than when the run was made in vacuo. Melts were examined in the usual way for the identification of phases. Certain of the melts were also examined by sectioning the molybdenum crucibles containing them.

Discussion of Experimental Data.

A selection of the heating and cooling curves obtained is given in Figs. 37 to 42.

Briefly it can be said that, with the addition of SiO_2 to to FeO there is a progressive depression of the temperature at which melting is complete. This is illustrated by the curves corresponding to the compositions 10%, 15%, and 20% of SiO_2. At the same time an invariant arrest appears at 1150°C. This conclusion is borne out very well by the cooling curves though the arrests occur at somewhat lower temperatures due to supercooling. In the case of the melt containing 10% of SiO_2 the completion of melting on heating appears to be very long delayed. This can probably be attributed to the presence of the iron rich phase produced by the dissociation of the free FeO on melting.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.



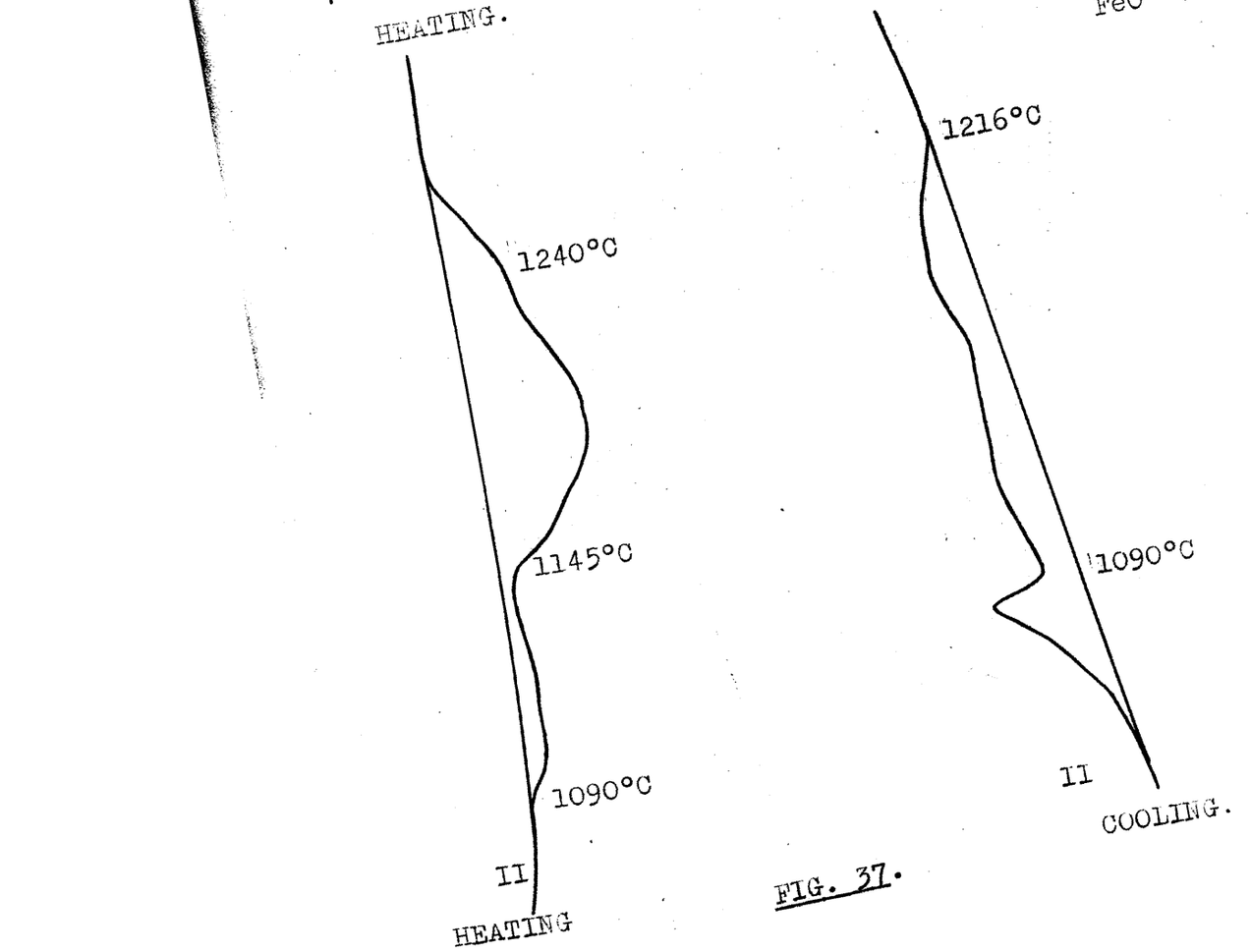


FIG. 37.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 20.
FeO : 80.

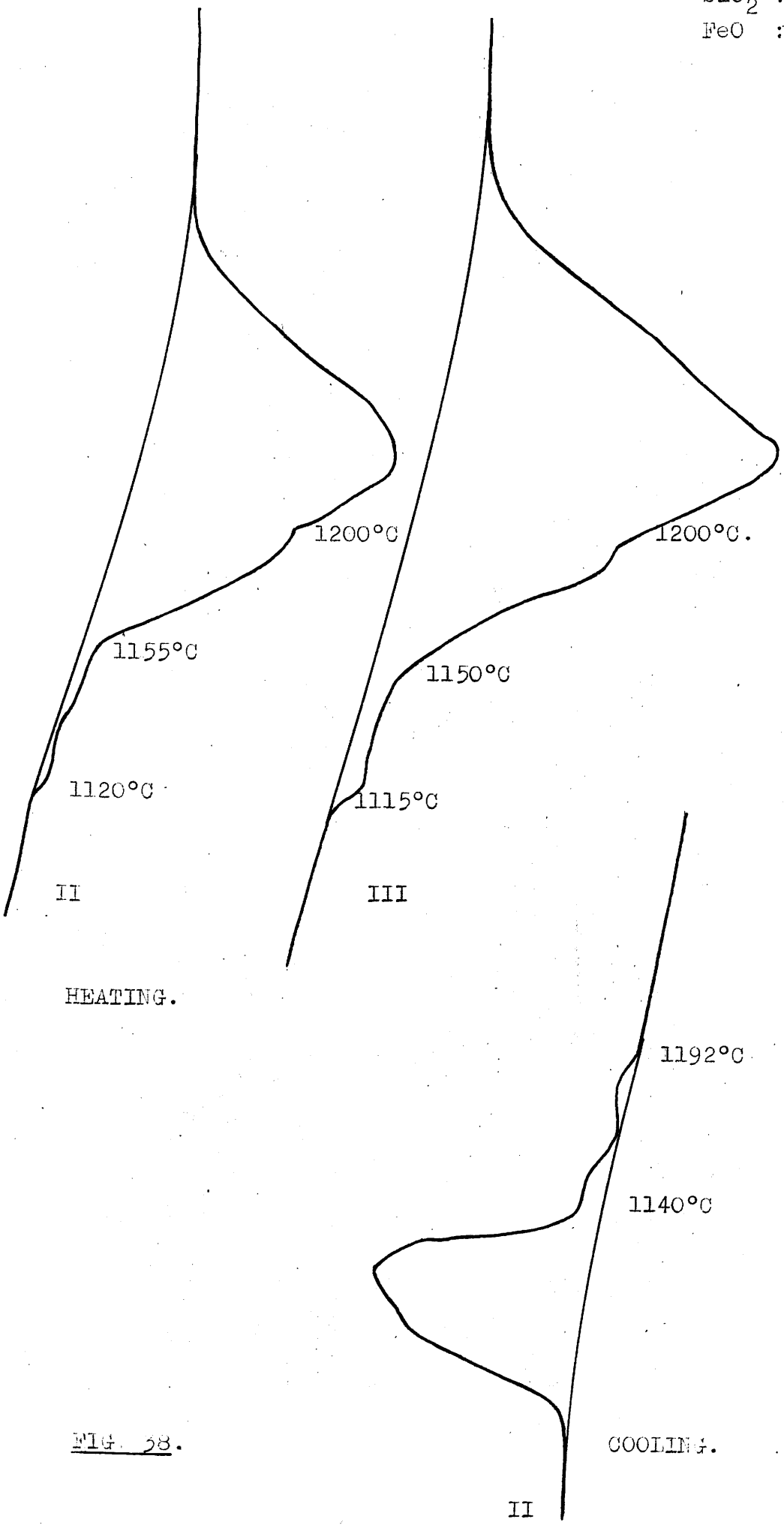
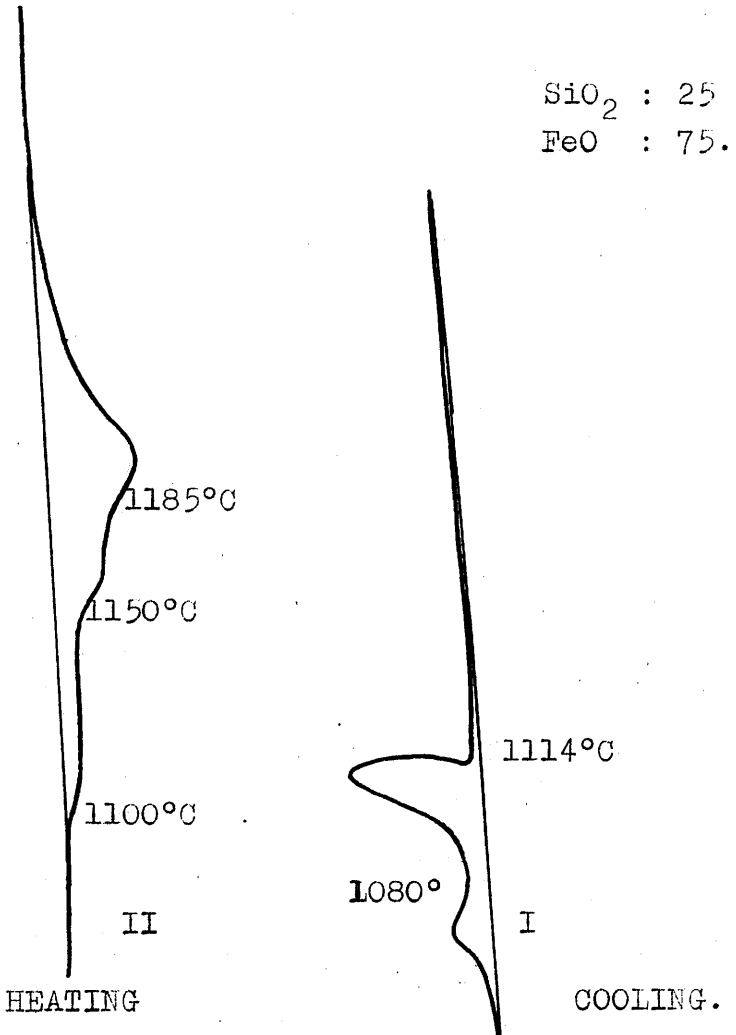


FIG. 38.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.



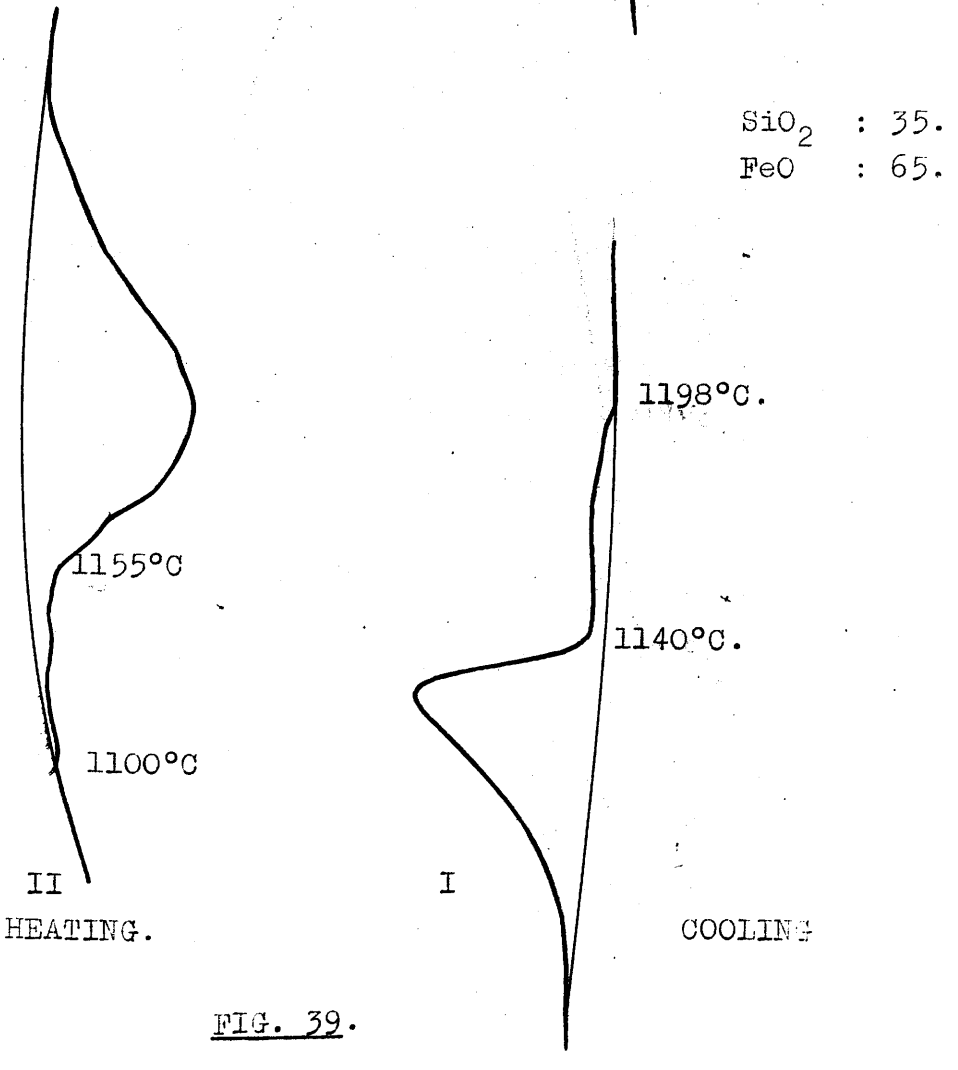


FIG. 39.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 30.
FeO : 70.

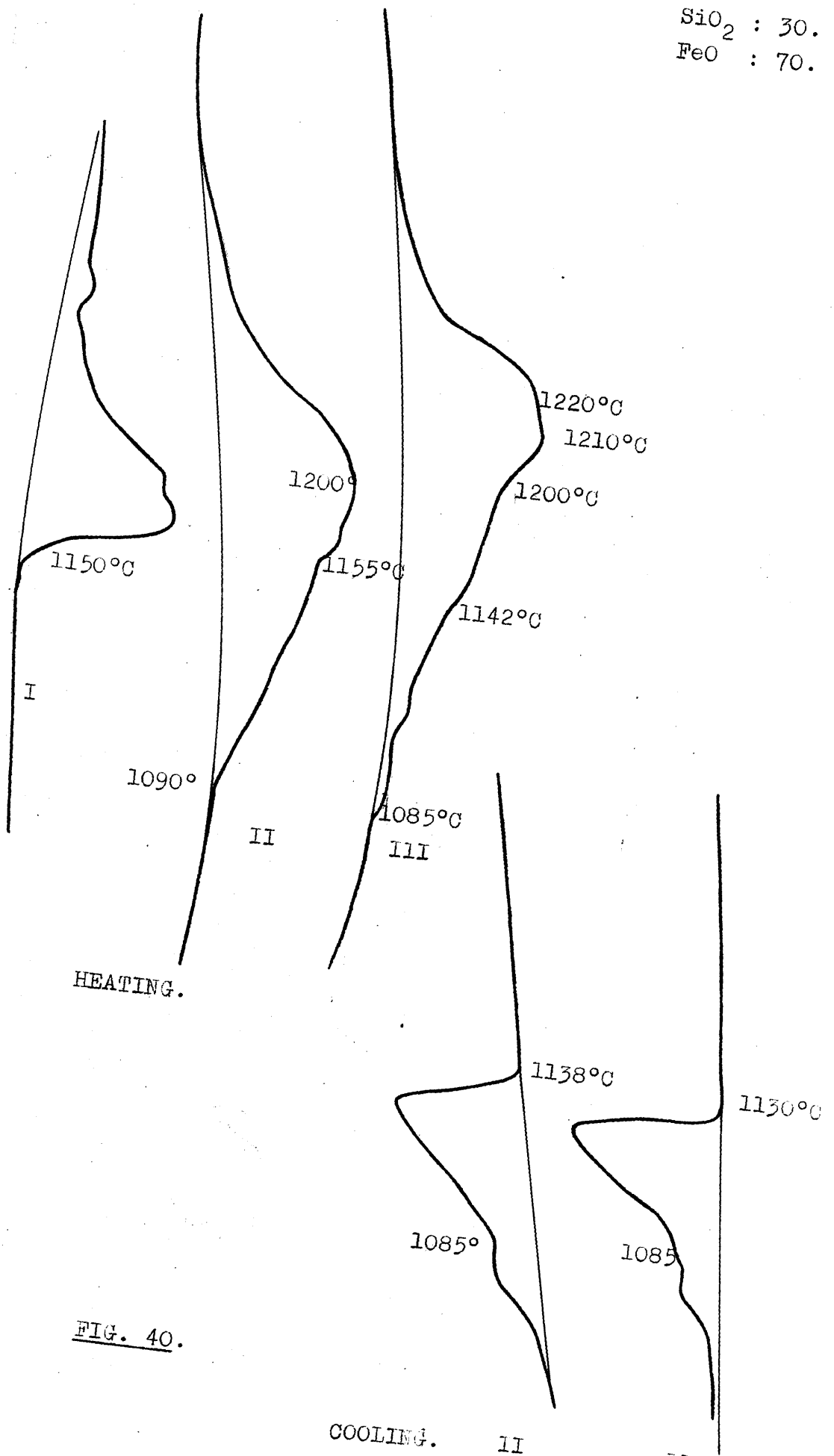
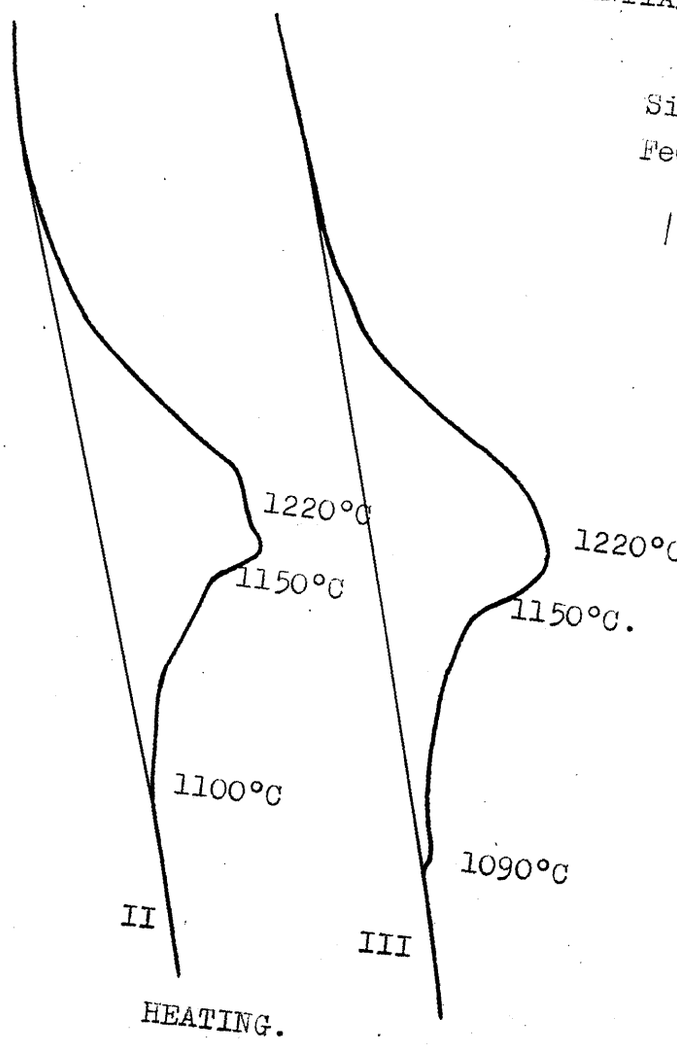


FIG. 40.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

SiO_2 : 40.
FeO : 60.



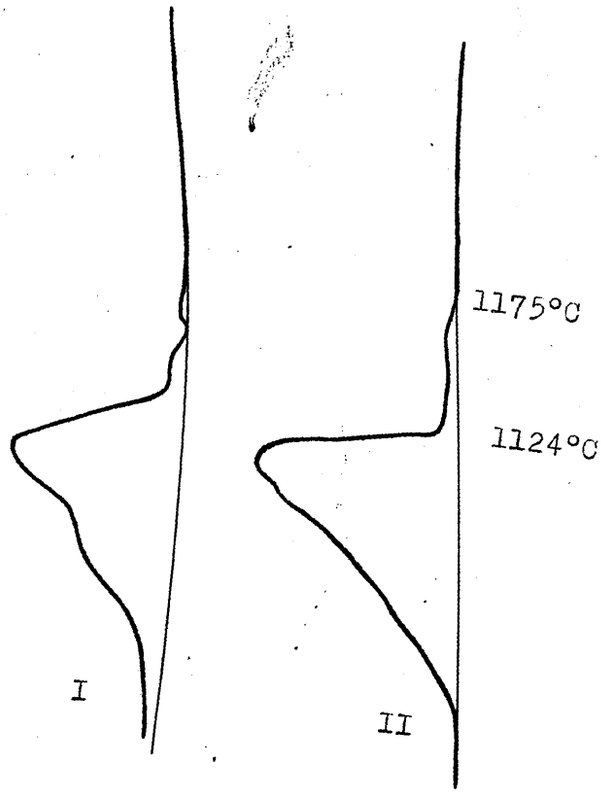


FIG. 41.

HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

(Reduced scale).

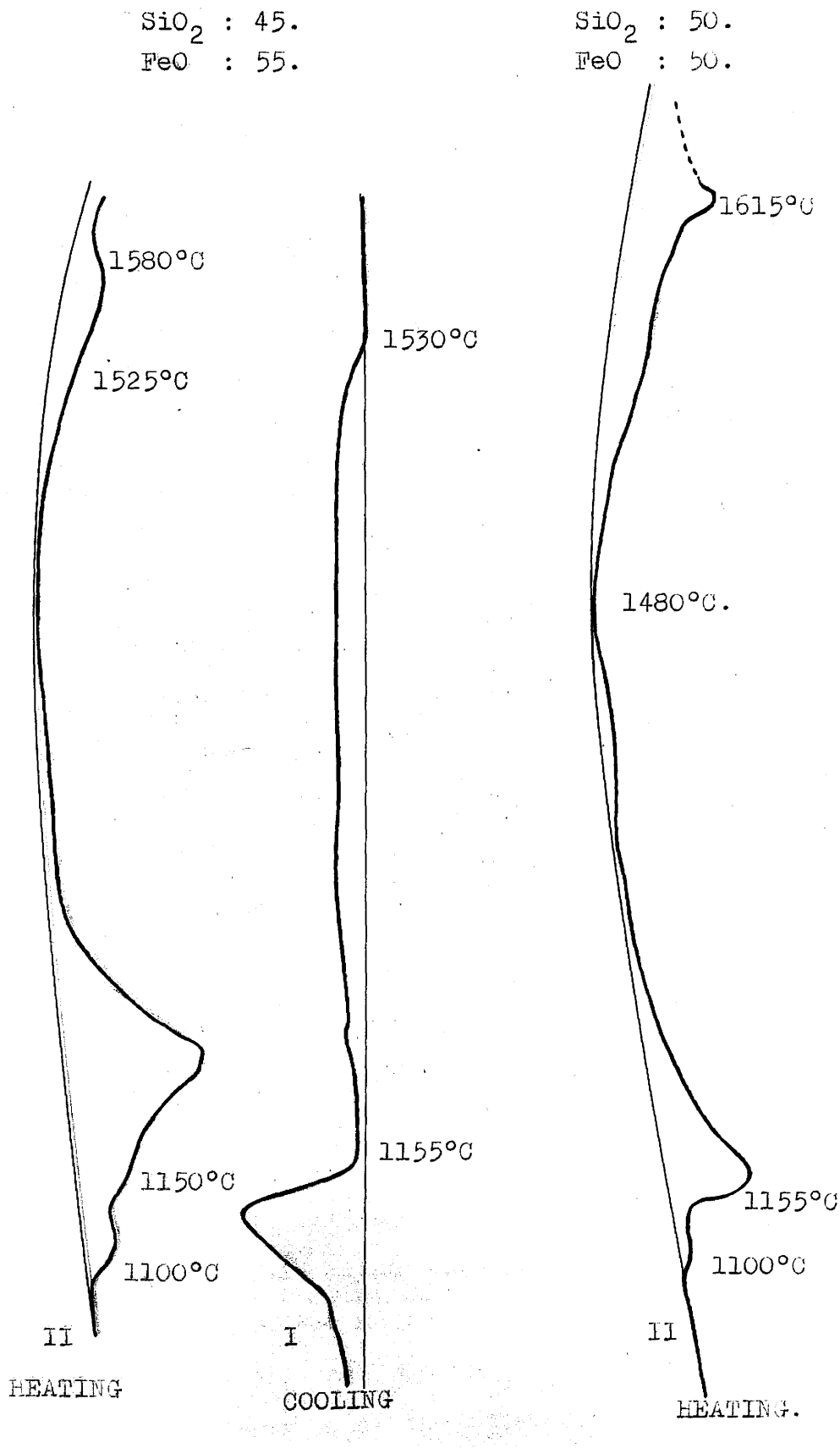


FIG. 42.

With 25% of SiO_2 the 1150°C point still occurs but the melting range is again longer.

A somewhat puzzling feature of these curves is that at a temperature of approximately 1100°C in all cases there is evidence of a change on heating involving absorption of heat. In many cases this took the form of a gradual drift of the spot of light from the galvanometer in the differential circuit, but it was of too constant occurrence to be the result merely of an accidental drift of the zero. Further though it was rather irregular it appeared on the whole to increase as the the fayalite composition was approached. In the case of the 30% SiO_2 melt (fayalite 29.4% SiO_2) it is so pronounced as to practically mask the beginning of melting. With higher percentages of SiO_2 it once more decreases in magnitude, though indications of it are present on all the curves reproduced.

With 30% of SiO_2 melting appears to be complete at 1210-1230°C. Increase of the SiO_2 content to 35% results in the appearence of an arrest at 1155°C, the liquidus arrest being placed at 1210°C. Thereafter with increasing SiO_2 content the arrest at 1155°C remains constant and is apparently the eutectic melting temperature. Incidentally it exists beyond the grünerite composition of 45% SiO_2, which would lead to the conclusion that grünerite could not exist. Over 40% SiO_2, however, the liquidus apparently rises very steeply and, by the time 50% of SiO_2, is reached, the mixtures are very infusible and very viscous, so that it is quite possible that even after melting a second time these melts would not be quite homogeneous, and so this alone was not taken as providing conclusive evidence on the matter. Curves for the compositions 45% SiO_2 ("grünerite"), and 50% SiO_2 are reproduced plotted on a reduced scale because of the extended temperature ranges they involve. During the investigation of the latter melt several attempts were made before the melt was completely fused. At last success was achieved but at a temperature of 1630°C approximately the "Pythagoras" tube fused so that the curve was

incomplete. As the melt had been completely molten, however, there seems little reasonable doubt that the bulge observed at 1615°C on the heating curve indicates the position of the liquidus. A mixture containing 60% of SiO_2 was found to be incompletely fused after heating to temperatures approaching 1600°C. Even after soaking at these high temperatures for a considerable time the arrest at 1155°C was still obtained on heating from low temperatures.

Optical Data: On examination of the above melts the occurrence of iron oxide and fayalite as phases was definitely established. In melts containing over 30% of SiO_2, however, it was found that there were apparently indications of three phases, fayalite of refractive index 1.78-2.00, cristobalite of refractive index 1.49 and traces of a phase with refractive index 1.74. A possible explanation was that grünerite did actually exist in the system $FeO-SiO_2$, but that, owing to the relatively rapid rates of cooling ,and the extreme viscosity of these melts, very little of it was actually formed on freezing. To settle the question several melts of the grünerite composition were made and cooled very slowly after soaking at 1600°C for periods up to three hours. The crucibles containing these were then sectioned and examined by reflected light. It was apparent that considerable amounts of cristobalite were present as shown by the characteristic dendrites in the form of skeletal octohedra and the ladder-like structure of the plates when seen in section. Under vertical illumination these appeared dark in a light background. Under oblique illumination they were seen to be clear and transparent while the background appeared greenish, and probably of duplex structure. Further examination of the powdered fragments revealed that in all probability the particles of refractive index = 1.74 previously described were duplex in nature and consisted of a fine-grained aggregate so that the refractive index measured was only an apparent one the effect observed being the sum of two separate effects. Hence no evidence pointing to the existence of grünerite in these

melts has been obtained, and it has been concluded that this material is not formed in the simple binary system FeO-SiO_2, at least under ordinary conditions of freezing. In the petrologically reported analyses of this material, various percentages of other oxides are invariably given as impurities, notably amongst these being MgO. It appears quite possible that these may be essential constituents of grünerite and that their presence is necessary to confer stability on it.

The Thermal Equilibrium Diagram: The thermal equilibrium diagram of this system has accordingly been constructed as in Fig. 43. Two eutectics exist (1) between FeO and fayalite at a composition containing approximately 24% of SiO_2 and melting at 1150°C, and (2) between fayalite and SiO_2 at approximately 39% of SiO_2 and melting at 1155°C. The configuration of the liquidus for FeO contents higher than 90% is only an approximation as FeO dissociates to give new phases. The region of immiscibility at the high SiO_2 end is taken from Greig's work and it fits in well with the rest of the diagram, which, on the whole, agrees fairly closely with that of Bowen and Schairer except that the two eutectic temperatures now quoted are somewhat lower than was indicated by them.

Grünerite is considered too unstable to exist. It will also be observed that the fayalite maximum is extremely flat and rounded, indicating a considerable amount of dissociation taking place on melting. It would seem, therefore, that even fayalite tends to be unstable at high temperatures. (In this respect it is of course acting in analogous fashion to tephroite and rhodonite which both undergo dissociation on melting.) With regard to the change observed on the heating curves in the neighbourhood of 1100°C, it is probable that this is concerned with fayalite as it appears to reach a maximum at the composition of this compound. No direct references to this change was found in any of the papers quoted above unless the extremely low values of 1075°C and 1115°C given for the two eutectic temperatures by von Keil and Damman can be attributed to this

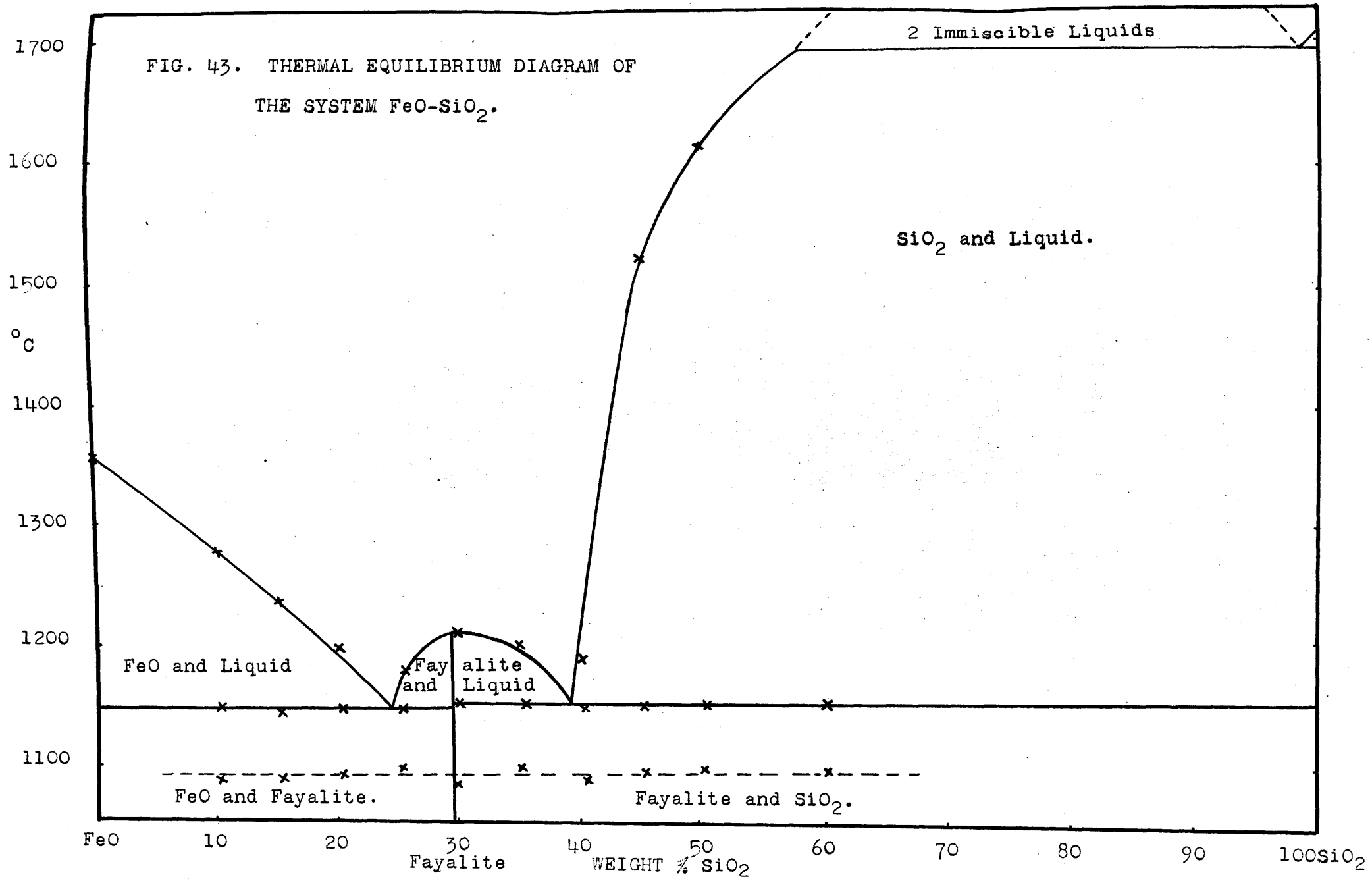


FIG. 43. THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM FeO-SiO_2.

cause. Esser, Averdiech, and Grass,[7] however, in their researches on the Specific Heats of materials at various temperatures have found that there is a marked increase in the specific heat of fayalite over 1100°C and have published a curve showing a marked break at 1105°C in the rate of increase of internal energy with temperature. They point out that this cannot be due to fusion taking place as no evidences of liquid formation were found until a temperature of 1195°C had been reached. Hence it seems probable that a change of some sort begins to take place in fayalite at approximately 1100°C. The exact nature of this change is not yet clear but it is not impossible that it may be connected with the increasing instability of this compound at high temperatures.

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PART I - SECTION 4.

THE CONSTITUTION AND PROPERTIES OF ACID SLAGS REGARDED ON THE BASIS OF THE TERNARY SYSTEM $FeO-MnO-SiO_2$.

The controlling influence of the slag on the reactions taking place in the open hearth furnace has long been recognized. Except for a certain amount of oxidation brought about by direct contact at the slag-metal interface, which can probably be regarded as fortuitous, the elimination of carbon, silicon, manganese, etc. is generally considered to take place by the action of the FeO dissolved in the molten metal, which gives rise to reactions of the type-

$$FeO + C = Fe + CO$$

and $$2FeO + Si = 2Fe + SiO_2$$

By virtue of its solubility in both media, the available FeO is partitioned between slag and metal according to the ordinary laws of solution (see McCance[1]). Further on account of its low solubility in the metal as compared with the slag, and since the proportionality expressed by the partition law must always be maintained, the slag can, in effect, act as a reservoir of FeO, maintaining a constant and regulated supply to the metal so that the oxidation reactions above proceed from left to right. The "availability" in this respect of the FeO in the slag at the temperature of the open hearth furnace is, therefore, a matter of importance since, from purely a priori reasoning, it might be expected that the presence of other constituents forming stable compounds with FeO would have considerable influence on its partition. A study of the effect of slag composition, and, in particular, of the constitution of slags in the liquid state might be expected to provide valuable information with regard to the functioning of the slag in this respect.

Again during the actual steel-making process, the effect of the atmosphere of the furnace cannot be neglected, and is probably of prime importance with regard to the supply of oxygen

to the metal. It is probable that oxidation of a certain proportion of the FeO of the slag to the ferric state is always proceeding, while the reduction of this Fe_2O_3, largely by contact with the metallic iron, serves to keep the FeO concentration from dropping as it ultimately would do as the reactions proceeded. The rate at which this oxidation and reduction cycle proceeds will depend, firstly, on the concentration of the "free" or "available" FeO in the slag, and, secondly, on the fusibility and fluidity of the slag, since these will exert a controlling influence on diffusion. The addition of oxide to the slag in the form of iron ore, mill scale, etc. is perhaps best regarded as a means of controlling this oxidation as it is probable that the indirect effect of a large increase of the FeO content with the consequent increase of fluidity brought about will outweigh the immediate effect of the addition of reducible oxide to the bath. It is well known that, other things being equal, the more fluid slag is always the more reactive. It is to be expected that both of these factors, oxidizability as well as fluidity, will depend largely on constitution.

Yet another aspect of slag study is provided by the problem of non-metallic inclusions in steel. The factors controlling the occurrence and distribution of these inclusions have been widely investigated because of the marked influence they may exert on the fatigue resistance and general mechanical properties of the metal. At the present moment complete elimination of these impurities is impossible, but to a certain extent the final form they take, and their distribution in the steel are capable of control. Such inclusions are of two kinds, "native" and "foreign". The latter are produced mainly by mechanical admixture of furnace slag and portions of refractory during the disturbances consequent on tapping and casting. In general they are relatively large in size and can be expected to rise fairly rapidly in the metal provided it is allowed to stand for some time in the fluid state. "Native" slag grains

on the other hand are inherent in the fluid metal and separate from it by virtue of reactions occurring in it (for example the oxidation of Mn, Si, etc. by the FeO in solution), or of changes in solubility taking place as the metal freezes. The addition of Si, Mn, or Al as deoxidisers to reduce the residual FeO in the metal also gives rise to solid or liquid products which contribute largely to the bulk of the inclusions. The materials so formed in the fluid steel will be very finely dispersed initially, but will, given sufficient time, tend to coallesce and rise to the surface. By reason of the imminence of freezing, however, this process will in ordinary practice be very incomplete. The factors controlling coallescence and elimination have been summarized by Benedicks and Löfquist[2]. Generally speaking the more fusible and fluid the material of the inclusion is the more rapidly will coallescence tend to take place, and therefore the greater are its chances of being removed before freezing occurs. On the other hand, products which are extremely refractory and of very low surface tension may remain so finely dispersed as to be harmless. By controlling the amount of deoxidiser added, and by using combinations of different deoxidisers, a measure of control over the composition and constitution of the resultant product can be obtained. The basis of such control is provided by the thermal equilibrium diagrams of the systems involved provided these are known with sufficient accuracy.

The Ternary System $FeO-MnO-SiO_2$.

As already pointed out acid slags consist essentially of the three oxides FeO, MnO, and SiO_2 with varying smaller amounts of Al_2O_3, CaO, Fe_2O_3, etc. Hence the ternary equilibrium diagram of the system $FeO-MnO-SiO_2$ must form the basis of any detailed study of these slags and their functions.

Benedicks and Löfquist[3] collected all the data then available and formulated a triangular diagram which was largely qualitative in nature. It is now possible to modify this diagram in the

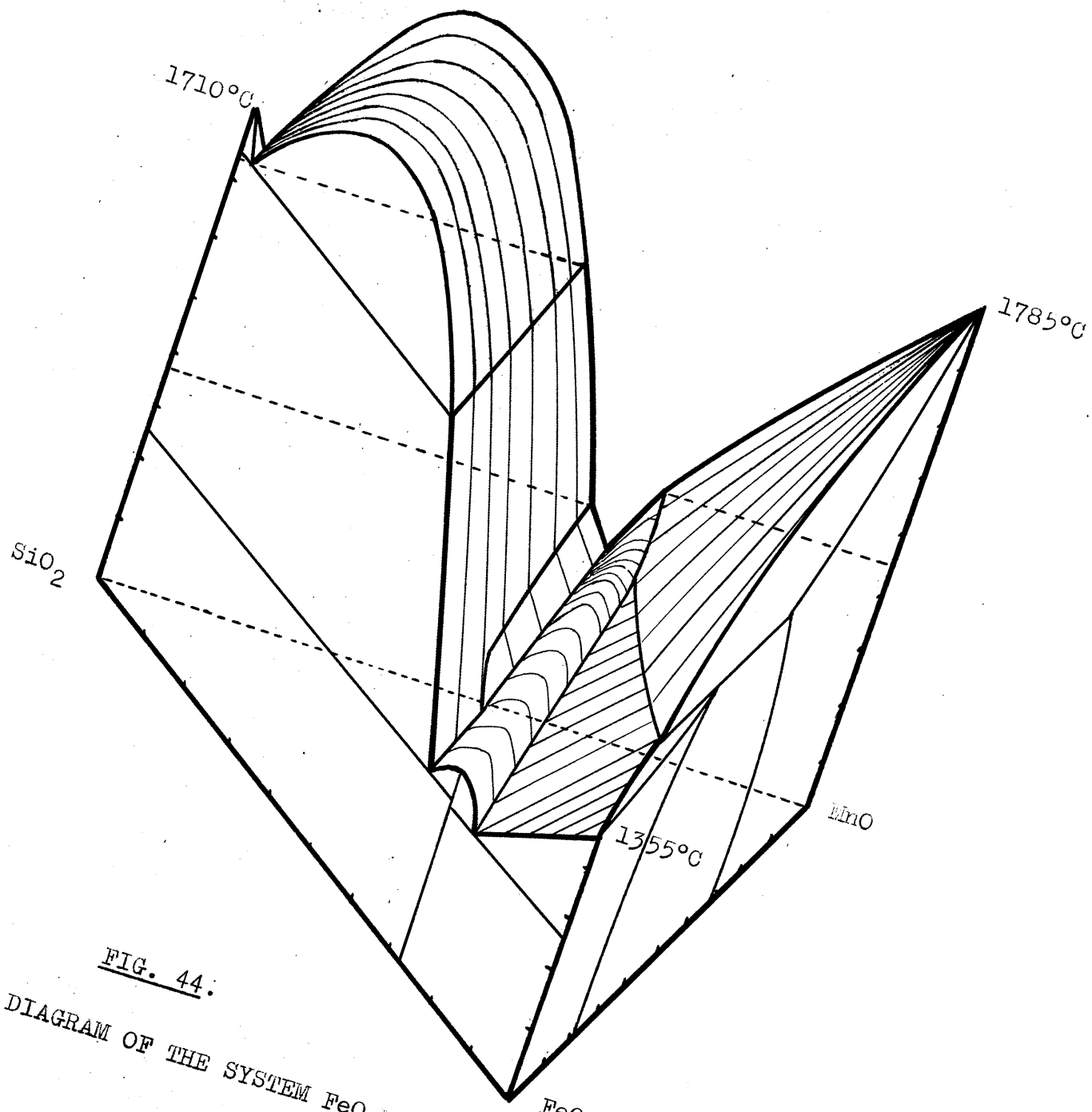


FIG. 44.

TERNARY DIAGRAM OF THE SYSTEM FeO-MnO-SiO_2.

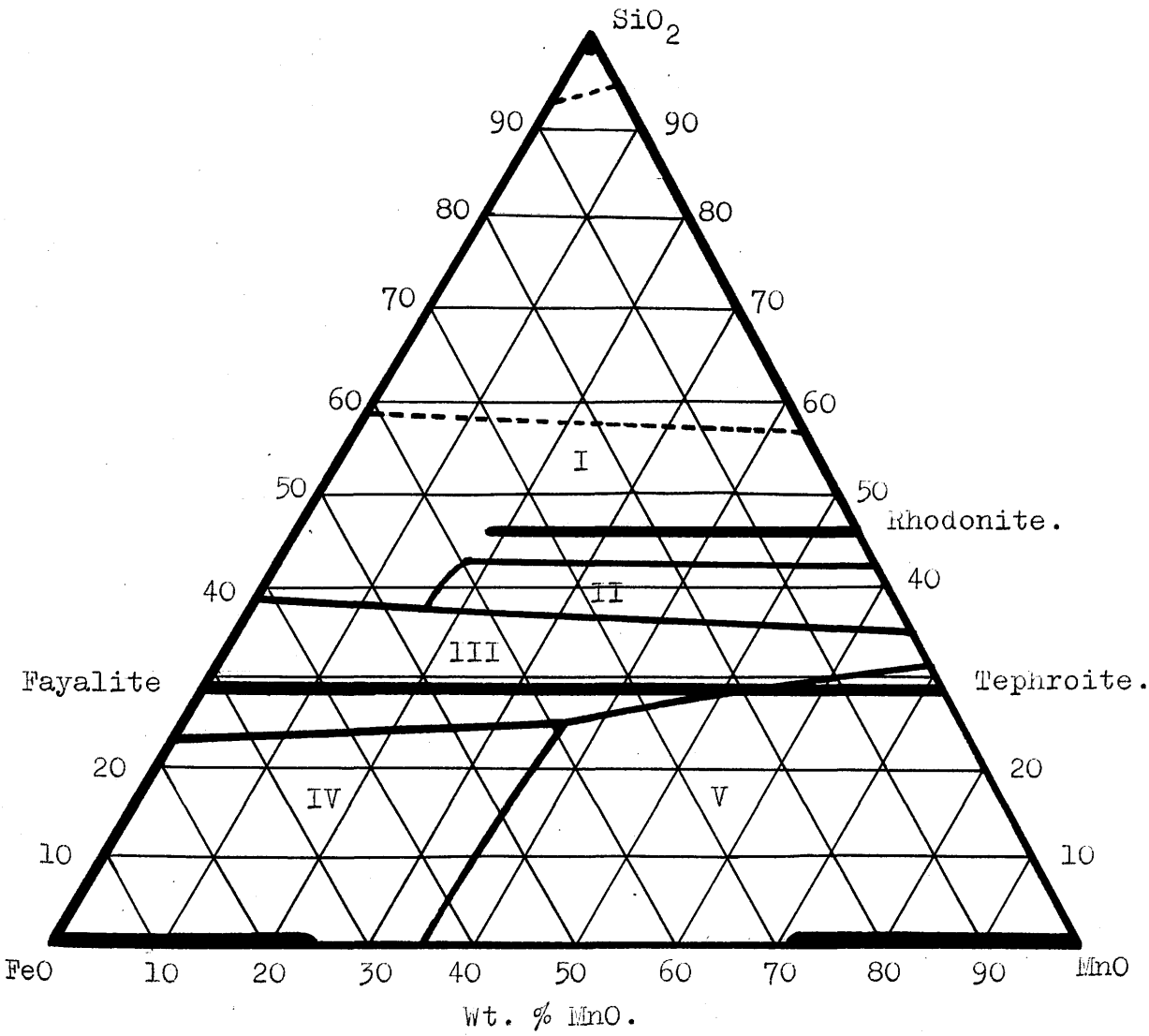


FIG. 45.

PHASE DIAGRAM OF THE TERNARY SYSTEM SYSTEM FeO-MnO-SiO_2.

PRIMARY PHASES OCCURRING.

I - SiO_2.

II - Rhodonite.

III- Fayalite, Knebelite, or Tephroite.

IV - FeO.

V - MnO.

HEAVY BLACK LINES INDICATE HOMOGENEITY RANGES OF SOLID SOLUTIONS.
BROKEN LINE INDICATES REGION OF IMMISCIBLE LIQUIDS.

light of the data provided by the present research. An isometric projection of the modified diagram is given in Fig. 44. Apart from the compenent binary systems already described this diagram is still to a considerable extent qualitative, at least with regard to the exact contours of the liquidus and solidus surfaces, as a systemmatic investigation of the melts has not yet been attempted. A number of qualitative observations on the melting of ternary mixtures have, however, been obtained, and further a considerable amount of optical data with regard to the phases occurring in various regions has been accumulated, and it is felt that a considerable degree of probability attaches to the diagram as it now stands. The optical data is summarized in the phase diagram reproduced in Fig. 45.

Discussion of the Ternary Diagram of the System FeO-MnO-SiO_2: The diagram now propounded differs from the original mainly in that grünerite does not occur, and that the supposed high melting point of fayalite (1503°C) has been replaced by the now fairly well established value of 1210-1220°C thus producing a general lowering of the ridge in the liquidus surface corresponding to the fayalite-knebelite-tephroite range of solid solutions. (Fayalite and tephroite, members of the olivine group, form a complete range of solid solutions. The name knebelite has been given to a 50:50 solid solution of the two. It is perhaps preferable to apply it to the complete series of such solutions to distinguish them from the pure components.) This incidentally is more in keeping with what has long been recognized by practical steel makers. As Bowen and Schairer[4] have pointed out, if the previous high figure were correct, slags of this composition would have to be avoided in practice, whereas in reality they are amongst the most fusible and fluid encountered.

As grünerite no longer appears, the eutectic trough running from 39% SiO_2 on the FeO-SiO_2 binary to the eutectic on the

$MnO-SiO_2$ binary may be expected to increase progressively in melting temperature from 1155°C to 1210°C as the MnO content increases. This is found to be highly probable since the melts over a considerable of this area begin to melt between 1160°C and 1180°C. Incidentally although grünerite itself cannot exist it will be observed that FeO can replace the MnO in rhodonite to a considerable extent. This is accompanied by a change in the characteristic red of rhodonite to a greyish colour. Whiteley and Hallimond[5] state that the limit of existence of rhodonite as a definite phase is reached when the ratio FeO/MnO = 73/27 which may be taken as indicating the limit to which FeO can replace MnO in the metasilicate molecule.

Between the fayalite-knebelite ridge and the free FeO or Wustite phase runs another eutectic trough and in this region also melting has been observed to begin in the region of 1170°C. This trough is, however, discontinuous since no eutectic exists between tephroite and MnO.

The only parts of this diagram which can be regarded as refractory at 1600°C are those corresponding to high MnO concentration and high SiO_2 concentration respectively. In acid practice where it is essential that SiO_2 should be in excess of the bases it is unlikely that the MnO concentration should ever be so high that an infusible slag would result from this cause. The liquidus surface corresponding to high SiO_2 content is important from this point of view, however, and it indicates that solid SiO_2 will be present at 1600°C in all ternary slags in which the SiO_2 content is greater than approximately 55%. Such slags would be expected to be very viscous and inert. Again the extreme steepness of the liquidus surface in this region indicates that a relatively small increase in the SiO_2 content of the slag could convert a fluid slag to a viscous one saturated with respect to SiO_2. The need for accurate control of highly silicious slags is therefore clear. The part played by oxide additions is also made clear in that they shift the composition of the slag to a more fusible region

of the ternary diagram. The diagram is, therefore, of considerable importance because of the information it conveys concern- the workable range of slag compositions.

Constitution and Functions of Acid Slags in the Fluid State:

The condition of the component oxides in composite slags in the fluid state is of great interest from the point of view of a study of the physical chemical relationships existing in the slag. In particular the condition of FeO is important because of the part it plays in the furnace reactions.

Consideration of the ternary diagram shows that the FeO in a ternary slag can only exist in the free state, in the combined state as a constituent of fayalite or knebelite, i,e. as orthosilicate,or in the combined state replacing some of the MnO in rhodonite, i.e. as metasilicate. Grünerite is apparently too unstable to exist even in the solid state. Further on melting, rhodonite is known to dissociate, at least in part (see the binary system $MnO-SiO_2$). The replacement of MnO by FeO with an unstable metasilicate may be expected to increase this dissociation. Again the maximum in the liquidus of the $FeO-SiO_2$ diagram corresponding to the fayalite composition is markedly flat. It is therefore probable that even fayalite undergoes a considerable amount of dissociation on melting. Tephroite also undergoes peritectic dissociation. Hence the presence of MnO can hardly be expected to have any marked stabilizing action on the orthosilicate molecule in the liquid state, so that knebelite also is likely to be at least partly dissociated. Hence it seems probable that even in the presence of excess SiO_2, with or without MnO, an appreciable amount of the total FeO will be "free".

Within recent years several investigators have carried out researches on the equilibria existing between the various constituents of the molten slag, and the conclusions arrived at are quite in keeping with these conceptions of slag constitution. Krings and Schackmann[6] have determined the equilibrium constant

of the reaction

$$FeO + Mn = Fe + MnO$$

at 1560°C in a system consisting of a slag of the mixed oxides over a bath of the molten metals, the concentrations of FeO and MnO being measured in the slag, and those of Mn and Fe in the metal. They have shown that the addition of SiO_2 to the melt of the mixed oxides causes an apparent displacement of this equilibrium to the right. The effect of SiO_2 addition will be essentially to form silicates of the two oxides, and this effect on the equilibrium constant can only be explained on Mass Action grounds if ferrous silicate is dissociated to a greater extent than manganese silicate. Incidentally the magnitude of the constant, even in the absence of SiO_2, is such that it is improbable that the reduction of MnO by metallic iron should ever proceed to any great extent in the open hearth process. Hence, since the solubility of MnO in molten iron has been shown to be negligible, this oxide cannot be regarded as an active agent in the oxidation of Carbon etc. from the bath, unless under very special circumstances.

Tamman and Oelsen[7] have obtained curves from actual furnace practice which agree with the conclusions of Krings and Schackmann. Again Korber and Oelsen[8] have investigated the partition of FeO between slags of varying content of FeO, CaO and SiO_2 and molten iron at 1575 to 1625°C and have found the concentration in the metal to depend only on the total FeO of the slag and to be practically uninfluenced by constitution. This would at once lead to the conclusion that, at the temperatures in question, the ferrous silicates of the molten slags were almost completely dissociated. Krings[9], in discussing these results, makes the statement that it is practically correct to regard all the FeO as "free".

Concerning the other aspect of slag activity, namely its oxidation by the atmosphere over the bath, it would be expected that constitution would play a considerable part in determining the extent to which it could proceed. Precise data is largely

lacking with regard to this property of the acid slag, but complete slag analysis, where available, invariably show the presence of a small proportion of Fe_2O_3 which tends to increase towards the end of the process when the reducing action of the metal bath falls off. Whiteley and Hallimond[5] estimated that at least half of the carbon removed between melting and tapping was removed by means of atmospheric oxygen transferred mainly through the slag. They also claimed to have shown that the equilibrium ratio of Fe_2O_3 to FeO in a given slag under given conditions of atmosphere and temperature depended on the SiO_2 concentration of the slag, decreasing as the SiO_2 increased. Under ordinary furnace conditions the Fe_2O_3 present during the boil was about .3%, but this increased to as much as 3% in some cases during the finishing stages. They state that, in the absence of reduction by metallic iron, the equilibrium amount would be about 4% in the ordinary acid slag. They therefore postulate an oxidation and reduction cycle in which Fe_2O_3 is formed and reduced continuously. In connection with this theory McCance[10] has pointed out that it is very unlikely that Fe_2O_3 as such will be formed under the conditions of temperature and pressure in the open hearth furnace. He describes the behaviour of an acid slag which was heated in a current of air at 1100°C and later up to progressively higher temperatures. At 1100°C it gained in weight an amount equivalent to the complete conversion of all the FeO present to Fe_2O_3 and the product was non-magnetic. On the temperature being raised to 1300°C, however, loss in weight took place, consequent on the decomposition of the Fe_2O_3 apparently and the product was magnetic. Fe_2O_3 as such dissociates readily at high temperatures by virtue of its high dissociation pressure. The presence of FeO resulting in the formation of Fe_3O_4 stabilises it, this latter compound having a very low dissociation pressure. Further it is to be expected that even after the destruction of the Fe_3O_4 lattice on fusion the Fe_3O_4 molecule will have some form of existence in the liquid state - in other words that the effect of constit-

ution will persist in the liquid state. Hence though Fe_2O_3 is formed and reported in chemical analyses it will presumably have no individual existence in either the liquid or solid slags, and Fe_3O_4 will properly speaking be the active agent in oxidation and reduction cycle. The actual amounts of Fe_2O_3 found in acid slags by Whiteley and Hallimond, even under equilibrium conditions and in the absence of metallic iron, are much smaller than could account for the complete conversion of all the FeO to Fe_3O_4. It is quite to be expected that an equilibrium will be attained in all cases between undissociated ferrous silicate, dissociated ferrous silicate giving free FeO and SiO_2, dissociated Fe_3O_4 resulting in free FeO and Fe_2O_3, and undissociated Fe_3O_4. The position of equilibrium would depend on the oxygen pressure in the atmosphere over the slag and on the SiO_2 contration of the melt. The dissociation relationships of the ferrous silicate would also be an important factor. So far no quantitative data are available. It may be noted in passing, however, that Schenck[11], Klarding[12] and their collaborators in their investigations on the equilibria between CO, CO_2 and the oxides of iron have found that the presence of excess SiO_2 causes the reduction of Fe_3O_4 according to the reaction

$$Fe_3O_4 + CO = 3FeO + CO_2$$

to proceed irreversibly, equilibrium being only attained when the conversion of all the iron oxide to FeO, corresponding to the formation of fayalite, is approached. Further reduction then proceeds with difficulty. This would indicate that the presence of SiO_2 decreases both the oxidisability and the reducibility of FeO. These experiments were, however, carried out on finely powdered solids at a temperature of 900°C and it is quite to be expected that fayalite would then be undissociated and stable. In the liquid state it is possible that a very different state of affairs exists.

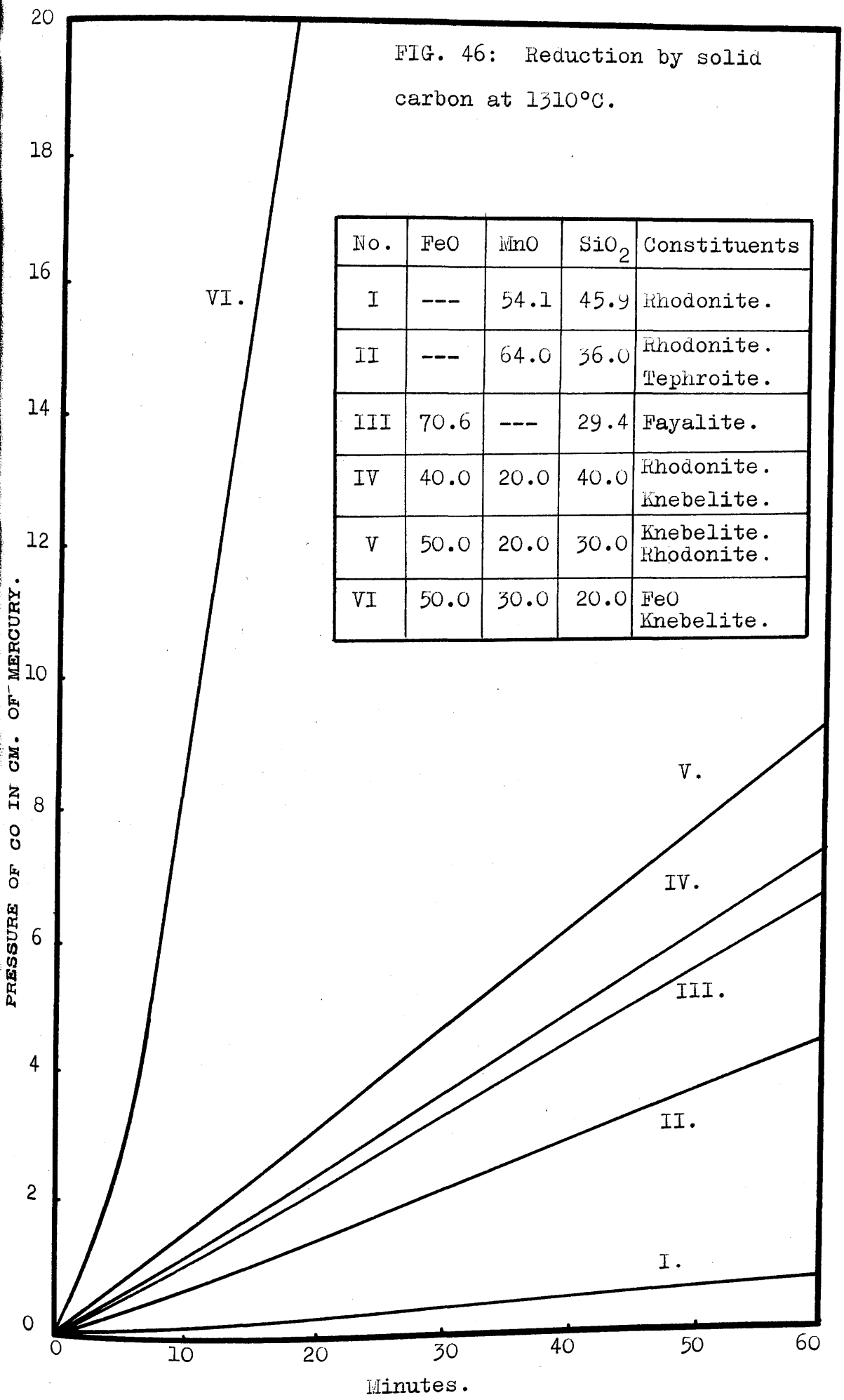
To try to arrive at something like a complete picture of slag relationships, and to correlate the work of the various

authors, a certain amount of work has been carried out along the lines indicated above, but as yet this is only in its preliminary stages. It has been found, for instance, that molten fayalite at temperatures in the neighbourhood of 1400°C undergoes a considerable amount of oxidation even at oxygen pressures as low as 2 to 3 centimetres of mercury. In addition, an attempt has been made to investigate the reactivity of various ternary slags. For this purpose the rate of reducibility by solid carbon was chosen since the progress of the reduction could readily be followed by measurement of the gases evolved, and because conditions could then be kept fairly constant throughout the different experiments. These were carried out in the apparatus described in Part II, Section 2 for the investigation of dissociation pressures. Melts were first prepared by melting the appropriate constituents in iron crucibles in vacuo. After cooling a small cylinder of carbon of constant weight and dimensions was added to each melt, which was then heated rapidly in vacuo to 1310°C when the temperature was held steady. Melts which would be completely fluid at that temperature were chosen and the pressure of gas generated in the tube was measured at constant intervals. Since reaction would occur at an approximately constant fluid slag-solid carbon interface this would give a measure of the rate of reaction. The results obtained are graphed in Fig. 46, details of the slags concerned being reported in the accompanying table. The constituents reported were determined in the various melts before carbon addition. Curve I is abnormal in that a certain amount of solid SiO_2 would be present at the temperature of the experiment, but a measure of the reducibility of a mixture of the two silicates of manganese is given by curve II. (NOTE: These curves are reproduced originating from a common zero. This was not actually the way in which they were obtained since varying small amounts of reduction took place during the initial heating to 1310°C.)

From consideration of the curves reproduced it is evident

FIG. 46: Reduction by solid carbon at 1310°C.

No.	FeO	MnO	SiO_2	Constituents
I	---	54.1	45.9	Rhodonite.
II	---	64.0	36.0	Rhodonite. Tephroite.
III	70.6	---	29.4	Fayalite.
IV	40.0	20.0	40.0	Rhodonite. Knebelite.
V	50.0	20.0	30.0	Knebelite. Rhodonite.
VI	50.0	30.0	20.0	FeO Knebelite.



that the activity does not depend on the concentration of the FeO, nor yet on the concentration of the SiO_2 or its complement the total concentration of FeO + MnO. Neither can the deviation from any such simple order be attributed simply to variations in fluidity. It is noteworthy, for instance, that knebelite (with a small amount of rhodonite containing FeO. See Curve V, Fig. 46: also Fig 45 for amounts and composition of phases.) is more reactive than fayalite (see Curve III, Fig. 46) though the FeO content of the latter is about equal to the total FeO + MnO content of the latter. Again rhodonite containing FeO (with a small amount of knebelite. See Curve IV, Fig. 46) is slightly more reactive than fayalite though the total MnO +FeO content is much smaller than the FeO content of fayalite. Further this melt being high in SiO_2 should be more viscous than the fayalite melt. (This statement is based on purely qualitative observations.) The relatively low reactivity of the pure manganese silicate melts (Curves I and II) and the very abnormal activity of the melt containing free FeO (Curve VI) seem to indicate that the FeO as such is the active agent in melts. If this is so then the effects of compound formation still persist to a considerable extent in the melts at 1310°C and the total content of FeO is probably not in the "free" condition.

Presumably the dissociation of the possible compounds will be subject to an equilibrium condition of the type

$$2FeO.SiO_2 = 2FeO + SiO_2$$

or $$MnO.SiO_2 = MnO + SiO_2$$

The presence of MnO may be expected to modify the dissociation relationships of ferrous silicate, and, conversely, FeO will affect the dissociation of the manganese silicates.

1310°C is not very far removed from the melting point of most of these slags and constitutional influences are likely to persist. At still higher temperatures dissociation may be expected to become progressively greater. That this is so appears to be shown by the work of the German investigators

already quoted.

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PART II.

RESEARCHES ON SOME OF THE CONSTITUENTS OF BASIC OPEN HEARTH FURNACE SLAGS WITH PARTICULAR REFERENCE TO THE OXIDISING MECHANISM OF SUCH SLAGS.

It is generally accepted that the elimination of carbon from the molten metal during the manufacture of steel takes place according to the homogeneous reaction

$$FeO + C = CO + Fe$$

which takes place wholly in the metal bath by virtue of the solubility of FeO (or oxygen) in the liquid steel. The concentration of FeO in the metal is, however, directly proportional to that of the FeO in the slag, and a definite partition coefficient exists connecting the concentrations in the two phases.

Of the terms on the right hand side of the above equation, the iron is present in very large excess and remains sensibly constant throughout the reaction. With regard to the carbon monoxide, after the initial small amount sufficient to saturate the metal has been dissolved, it must escape to the atmosphere over the bath, being thus removed from the sphere of reaction. Hence as both terms on the right hand side remain constant throughout the reaction, the conditions at equilibrium must be expressed by the relationship

$$K = (FeO).(C)$$

where (FeO) and (C) are the concentrations of these substances in the metal, and K is a constant for any given temperature.

During the initial stages of the process the conditions are necessarily far removed from equilibrium, and the reaction goes from left to right with elimination of carbon, a constant supply of FeO being maintained from the slag. Towards the end of the operation, however, when the carbon concentration has fallen to a low value, equilibrium conditions should be approached. Carbon removal should then take place much more

slowly, and the FeO concentration of the metal should rise slightly until no more diffusion of FeO from the slag to the metal takes place, and it is in equilibrium with the FeO of the slag on the one hand and the carbon concentration of the metal on the other. Reaction would then cease.

This state of affairs can be realised in the acid process, where the slags are essentially acid in nature and contain excess of free silica (though in practice the furnace is usually tapped with the carbon still falling slowly). The product (FeO).(C) then reaches a constant value. In basic practice, however, an entirely different condition exists. Towards the end of the process, the carbon begins to be eliminated with increasing rapidity, and it is found that the reason for this is an abnormal increase of FeO in the metal, so much so that the product (FeO).(C) is actually increasing rapidly when the furnace is tapped. Decreasing the supply of air in the furnace gases can reduce the magnitude of this effect considerably. To quote McCance[1], "In the acid process, control at the end of the operation is almost automatic; in the basic process the state of the metal at the end is materially affected by the air (oxygen) in the atmosphere over the bath."

This phenomenon has been explained by McCance and others in the following way. Though ferric oxide itself is unstable at high temperatures, the presence of lime as in these basic slags causes the formation of calcium ferrites which are stable under the conditions prevailing in the furnace. In a strongly basic slag, therefore, under an oxidising atmosphere the lower oxides of iron will tend to become oxidised to the ferric state with formation of ferrites. The ferrite content of the slag is, however, kept from increasing by the reducing action of the iron and, indirectly, the carbon of the metal bath. The ferrites, therefore, or more correctly, the iron oxide of the slag by undergoing a continuous cycle of oxidation and reduction, acts as an oxygen carrier to the metal bath. In the earlier stages of the process, the carbon of the bath by virtue of its

greater"affinity" for oxygen, is in effect the chief medium for this reduction, but towards the end of the process, when the carbon content is low, the reduction of the ferrites is mainly by the metal itself. This will at once result in the formation of more FeO in the metal and slag, with a consequent increase in the rate of formation of ferrites. The FeO content of the slag and metal will thus towards the end of the process increase "in snowball fashion" with the effect already noted.

The most obvious means of control is to decrease the oxidising power of the furnace gases. Reagan[2] has stated that the addition of silica to the slag has a similar effect. The explanation would appear to be that the increase in acidity decreases the stability of the ferrites, or that the formation of calcium silicate by decreasing the concentration of free lime reduced the velocity of the ferrite-forming reactions.

The theory advanced above, therefore, fits the facts quite well, but it had never been completely verified by actual experiment, so that it was felt to be highly desirable that an attempt to do this should be made. The work carried out in this connection can conveniently be divided into two sections: Section 1 - The determination of the thermal equilibrium diagram of the system $CaO-Fe_2O_3$, and Section 2 - An investigation into the dissociation pressures of ferric oxide and the ferrites at high temperatures.

PART II - SECTION 1.

THE THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM $CaO-Fe_2O_3$.

Ferric oxide, like alumina, possesses amphoteric properties, and can act as an acid towards strongly basic oxides. For instance with lime, calcium ferrites are produced. Several ways of producing these are described in the literature. (See Gmelins Handbuch der Anorganische Chemie[3]), for example, by heating mixtures of Fe_2O_3 with CaO, $Ca(OH)_2$, $CaSO_4$, or $CaCO_3$ at temperatures ranging from 600°C to 1100°C in air, or, in the wet way, by precipitation from a solution of ferric chloride with excess of lime water.

The thermal equilibrium diagram of the system $CaO-Fe_2O_3$ has also been investigated by several workers and various possible forms have been suggested. Probably the earliest was that of Hilpert and Kohlmeyer[4] who proposed a diagram in which no fewer than five compounds between the two components occurred. Sosman and Merwin[5], in a much more recent investigation, found only two compounds, monocalcium ferrite ($CaO.Fe_2O_3$) and dicalcium ferrite ($2CaO.Fe_2O_3$). Their diagram was left incomplete at the Fe_2O_3 end as it was found impossible to prevent the formation of a considerable amount of ferrous iron with melts in this region. With regard to the melting point of Fe_2O_3, Kohlmeyer[6] found that pure sintered oxide, when heated rapidly in a stream of oxygen to reduce the dissociation to a minimum, melted at 1565°C. Even with these precautions, however, there must have been a considerable proportion of Fe_3O_4 present at the melting point.

Campbell[7] and Hansen and Bogue[8] from their researches on the constitution of Portland cement confirm the existence of only two compounds as found by Sosman and Merwin. Nicken and Grünewald[9] on the other hand claim in addition to have prepared a third with the formula $5CaO.3Fe_2O_3$.

Hence there still existed a degree of uncertainty concerning this system, and it was thought desirable to redetermine it,

and incidentally to obtain fresh data on the properties of the melts.

PREPARATION OF MATERIALS.

Preparation of Fe_2O_3: The most satisfactory preparation of pure Fe_2O_3 was found to be from the decomposition of pure ferrous oxalate under correct conditions. For this purpose the ferrous oxalate was heated at a slow rate in an alundum boat in an evacuated "Pythagoras" tube. The decomposition was allowed to proceed at the lowest possible temperature to ensure the production of the highly reactive form of Fe_2O_3 - the so-called pyrophoric form. During the process of decomposition the gases were continuously removed from the furnace by a "CENCO Hyvac" pump. When decomposition was complete, as indicated by the cessation of gas evolution, the furnace was cooled to 400°C and oxygen admitted slowly. Vigorous oxidation of the FeO to Fe_2O_3 occurred accompanied by the evolution of heat, which was frequently sufficient to raise the temperature by 200°C, and if the temperature of the mass before oxygen admission had been too high , a sintered mass containing much Fe_3O_4 was obtained. The oxygen pressure was allowed to rise to approximately one and half atmospheres, and after a short soaking at 600°C the material was allowed to cool in the tube to room temperature.

Each batch of Fe_2O_3 so prepared was tested for the presence of ferrous iron by testing colorimetrically using an ammoniacal solution of dimethyl-glyoxime. The colour of Fe_2O_3 varies considerably and appears to depend upon the temperature during oxidation. Sometimes there was a marked variation in colour in the same batch, indicating a temperature gradient over the length of the boat. The colour generally varied from reddish brown to slate colour. On one occasion the product was orange in colour and was strongly magnetic, though no trace of ferrous iron could be detected. This material was more readily soluble

in hydrochloric acid than the usual product, and was undoubtedly the magnetic low temperature modification of Fe_2O_3 mentioned in the literature.

Preparation of CaO: CaO was prepared from pure calcium oxalate by decomposing it in a platinum basin at a temperature of 1000°C. The product was tested before use to ensure the absence of CO_2.

EXPERIMENTAL PROCEDURE.

Preliminary work was carried out to determine the conditions necessary for the formation of the ferrites. It was found necessary to employ platinum crucibles, all other materials tried causing reduction of the ferric oxide. (The ordinary refractory materials were unsuitable as they tended to slag with the melts.) Further it was observed that, if CaO and Fe_2O_3 in the proportions to form $CaO.Fe_2O_3$ were heated up at normal rates to 1250°C in air, no compound was formed, and the mass remained unfused. If, however, the finely ground mixture was maintained at 1000-1100°C for a few hours a dark powder was obtained in which no free lime could be detected. After heating this powder further to 1250°C it was found that fusion had occurred, and, on cooling, a mass of hard, black, metallic-looking needles was formed. Apparently Fe_2O_3 becomes unstable in air at temperatures round about 1200°C, and, under the first conditions of heating, decomposition took place more rapidly than combination with the lime so that no compound was formed and the mass remained infusible at 1250°C. At 1000°C, however, Fe_2O_3 is stable in air and can react slowly with the finely divided lime in the solid state to form the compound, which remains stable over 1200°C, and melts to give the characteristic needles of monocalcium ferrite.

On heating in a "Pythagoras" tube under oxygen at a pressure of approximately one and a half atmospheres, the compound was formed even on rapid heating. All melts for this system were therefore carried out in "Pythagoras" tubes under oxygen pressure.

The furnace employed was of the molybdenum wound type already described, the arrangement of the apparatus being as shown in Fig. 26, Part I. Under these conditions it was necessary to use platinum for both the crucible and the blank, and a platinum/platinum-rhodium thermocouple was employed for temperature measurement. For the differential thermocouple the system platinum/platinum-rhodium/platinum was made use of. In the earlier experiments attempts were made to immerse the point of the temperature measuring thermocouple in the melts, but trouble was experienced due to the great tendency of many of the melts to "creep" up the wires and attack the silica insulation, causing erratic behaviour of the thermocouple and contamination of the melts with silica. Finally the thermocouple points were attached to the outside of the crucible, after this had been shown by trial to give satisfactory results. Owing to the relatively large size of the crucibles employed melts of 15 grams could be investigated, and hence marked arrests were obtained on the ordinary time-temperature curves as well as on the differential curves. For all the melts belonging to this system, therefore, differential and time-temperature (inverse rate) curves were taken simultaneously.

The various melts were prepared by grinding together in an agate mortar the requisite amounts of CaO and Fe_2O_3. In all cases first heat curves are of these mechanical mixtures and differ somewhat in contours from subsequent curves. After the determination of the thermal data, tests were made for the presence of ferrous iron, and, except in the case of those mixtures containing Fe_2O_3 as a free phase, this was never present as more than a trace. Finally the optical properties of the phases present in each melt were determined by the Becke method as already described in Part I.

Heating and Cooling Curves: A selection of the differential and inverse rate time-temperature curves taken as described above is given in the accompanying diagrams. In interpreting the time-temperature curves it should be remembered that the

thermocouple was attached to the outside of the crucible and hence that it is probably more nearly correct to take the beginning of the time lag rather than the position of maximum deviation as indicating the temperature of change. The curves for those melts which contained less than approximately 80% of Fe_2O_3 call for no further comment as the method of interpretation is sufficiently clear, and no anomalies occur. Whenever Fe_2O_3 was present much in excess of the proportions required to form $CaO.Fe_2O_3$ irregularities began to arise, as large thermal arrests of a very ill-defined and uncertain type appear at temperatures a little above those at which melting begins. It was known that these were actually occurring in some cases at temperatures when the material was completely molten. Incidentally they rendered the determination of the true liquidus very uncertain. It was found that all these melts, on cooling at ordinary rates contained considerable amounts of ferrous iron, but, before the dissociation pressures had been investigated, the exact nature of these arrests remained obscure. However the dissociation determinations on mixtures of Fe_2O_3 and CaO indicate that they correspond quite closely (allowing for the relatively rapid rates of heating and cooling) with the temperatures at which rapid dissociation of the Fe_2O_3 might be expected to take place under oxygen pressures of one and a half atmospheres, the pressure maintained in the tube throughout these experiments. It was also found during the later part of the work that, when Fe_2O_3 was in equilibrium with its own oxygen pressure at high temperatures, any decrease of the oxygen pressure of the system caused a considerable fall in temperature of the mass, while, conversely, the admission of oxygen to the partly dissociated oxide caused a marked rise. From a consideration of the dissociation curves of the calcium ferrites, it seems probable that, even with CaO in excess of the composition $CaO.Fe_2O_3$, a small amount of dissociation would occur on melting, although this, by virtue of the action of the lime would be much smaller than in melts containing free Fe_2O_3.

HEATING CURVES - DIFFERENTIAL METHOD.

CaO : 45

Fe_2O_3 : 55.

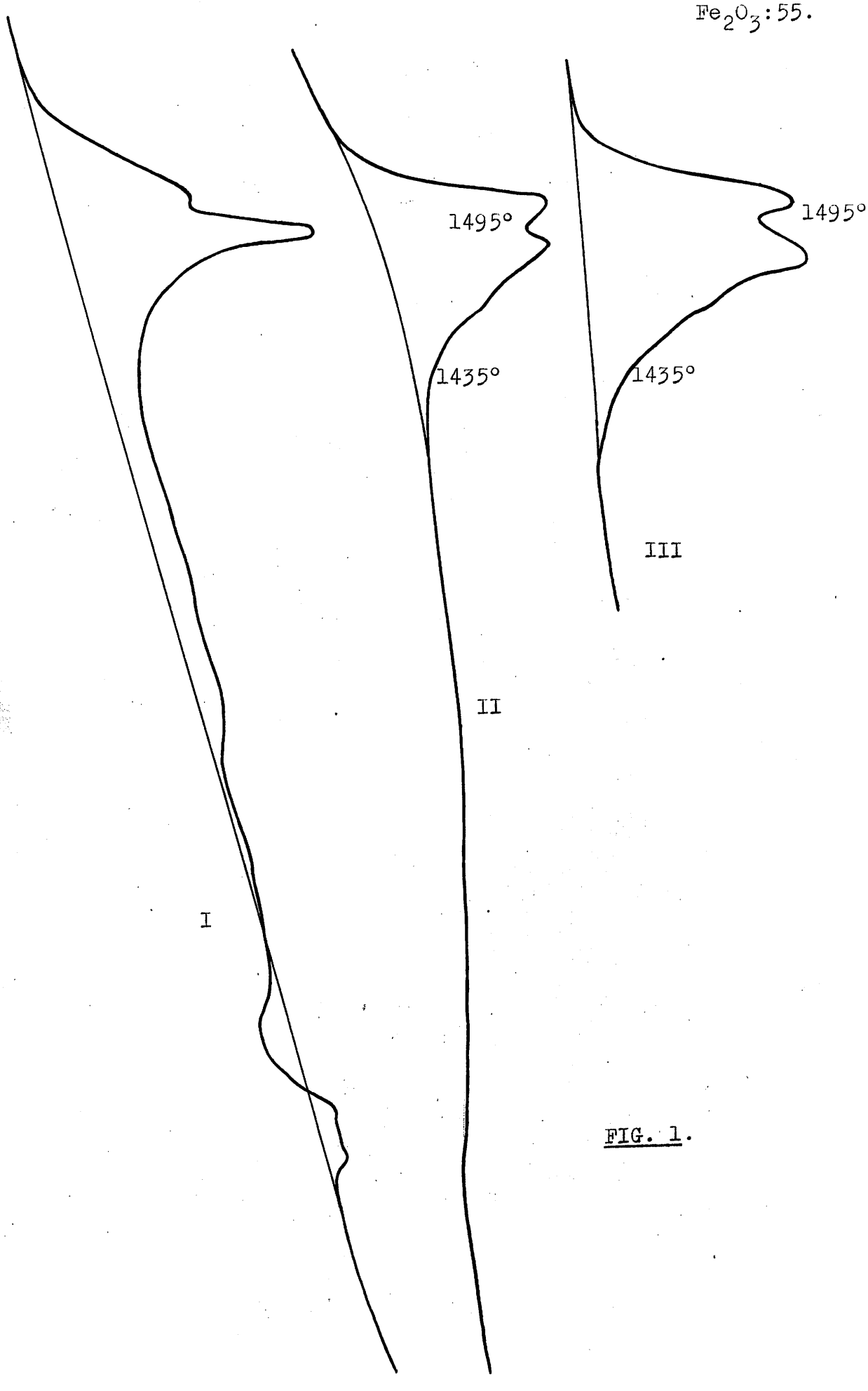


FIG. 1.

COOLING CURVES - DIFFERENTIAL METHOD.

CaO : 45.

Fe_2O_3: 55.

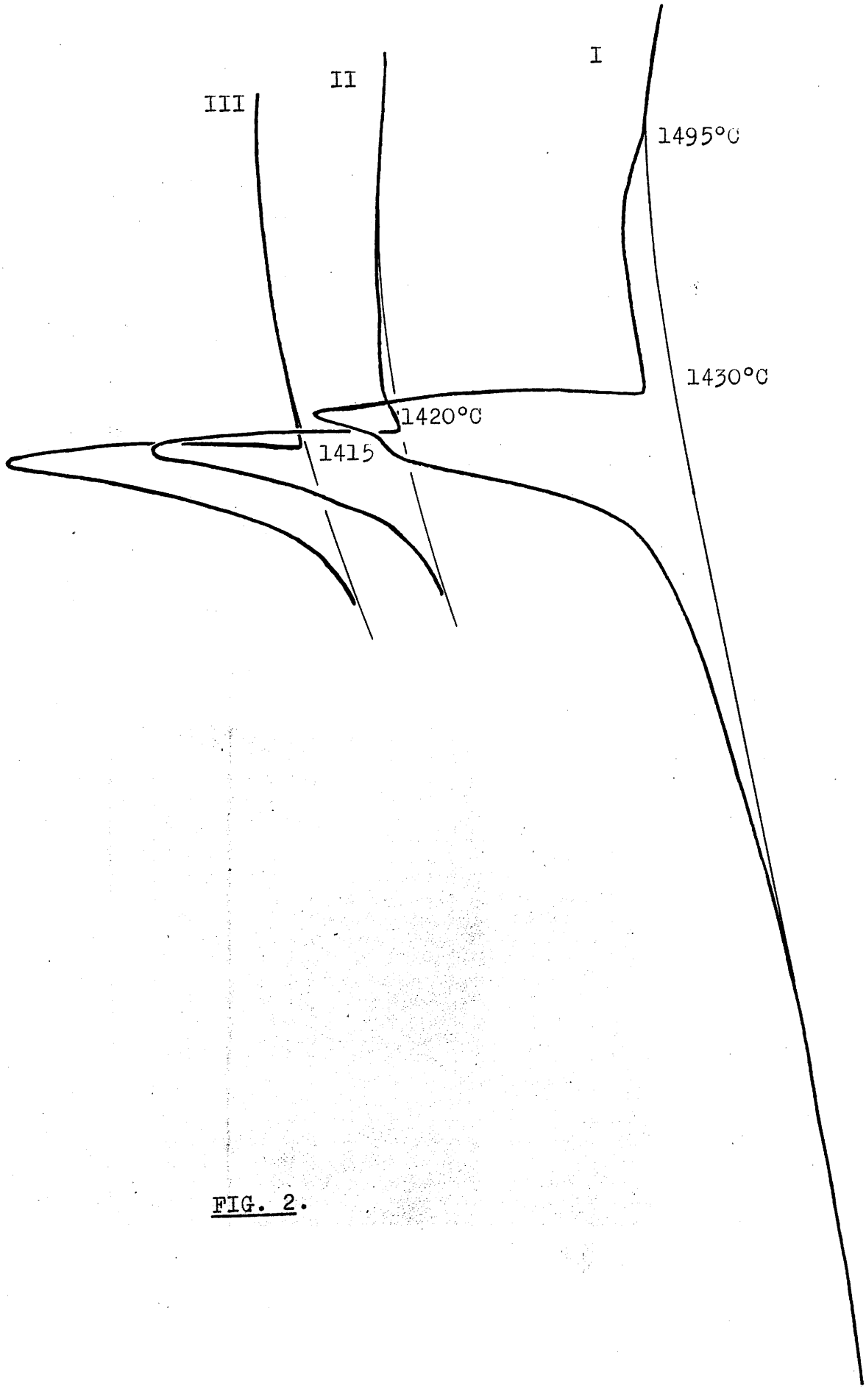


FIG. 2.

CaO : 45.

Fe_2O_3 : 55.

HEATING CURVES - INVERSE RATE.

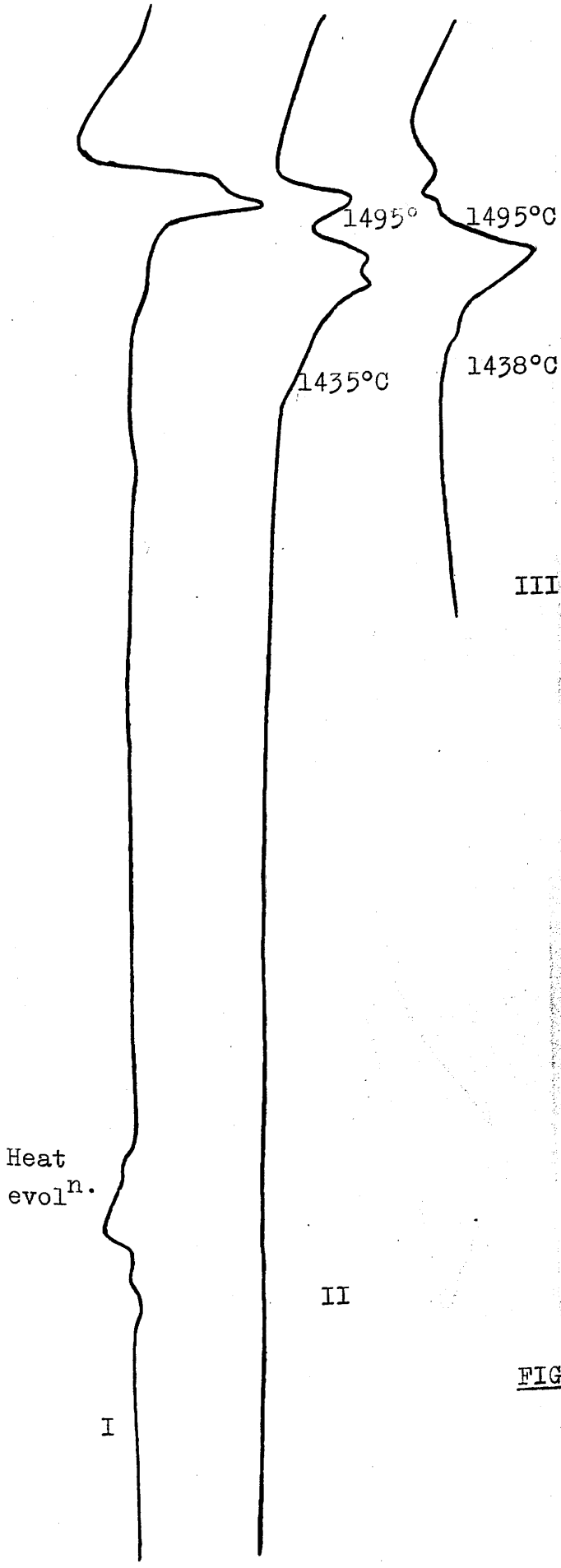


FIG. 3.

HEATING CÚRVES.

CaO : 41.

Fe_2O_3 : 59.

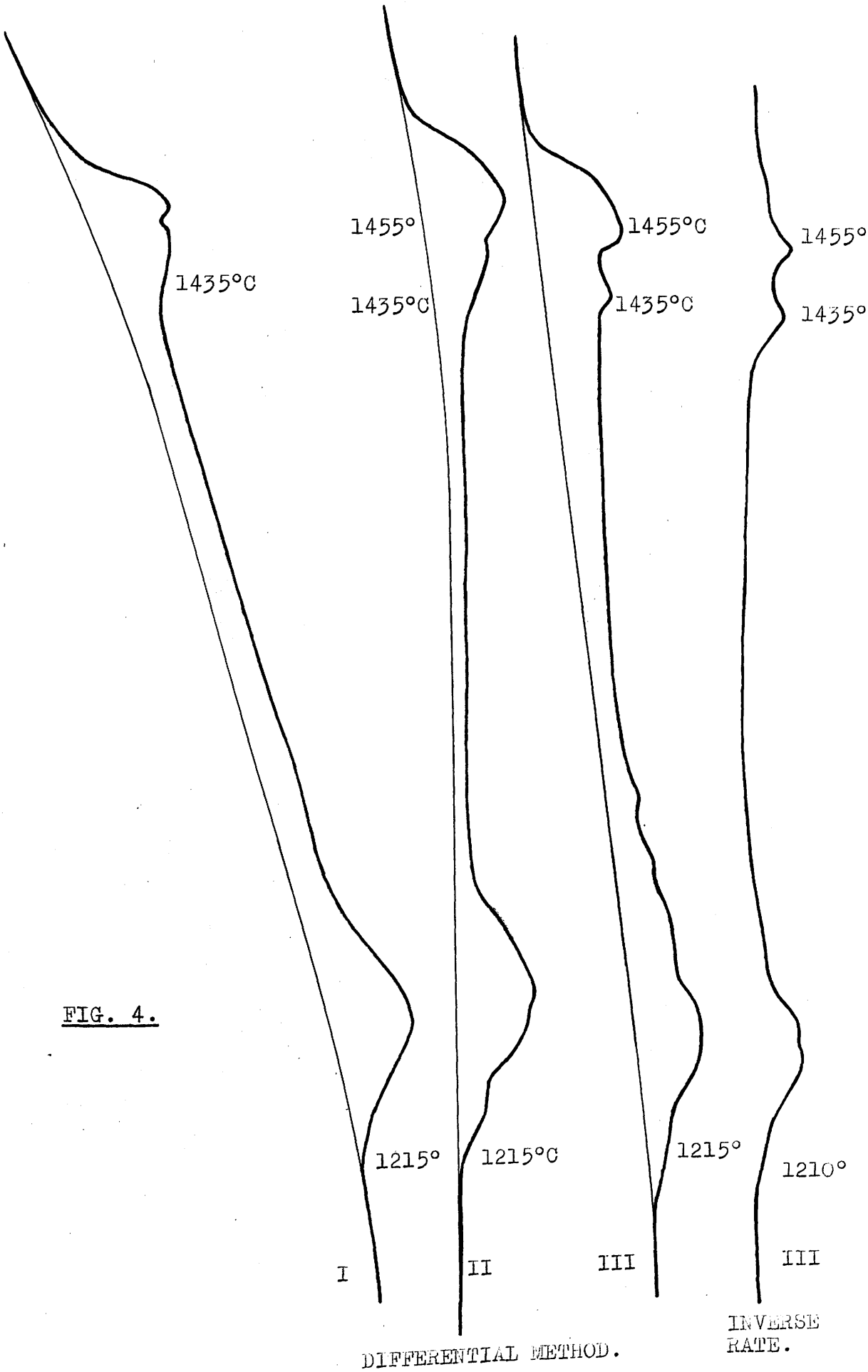


FIG. 4.

DIFFERENTIAL METHOD.

INVERSE RATE.

CaO : 41.

Fe_2O_3 : 59.

COOLING CURVES.

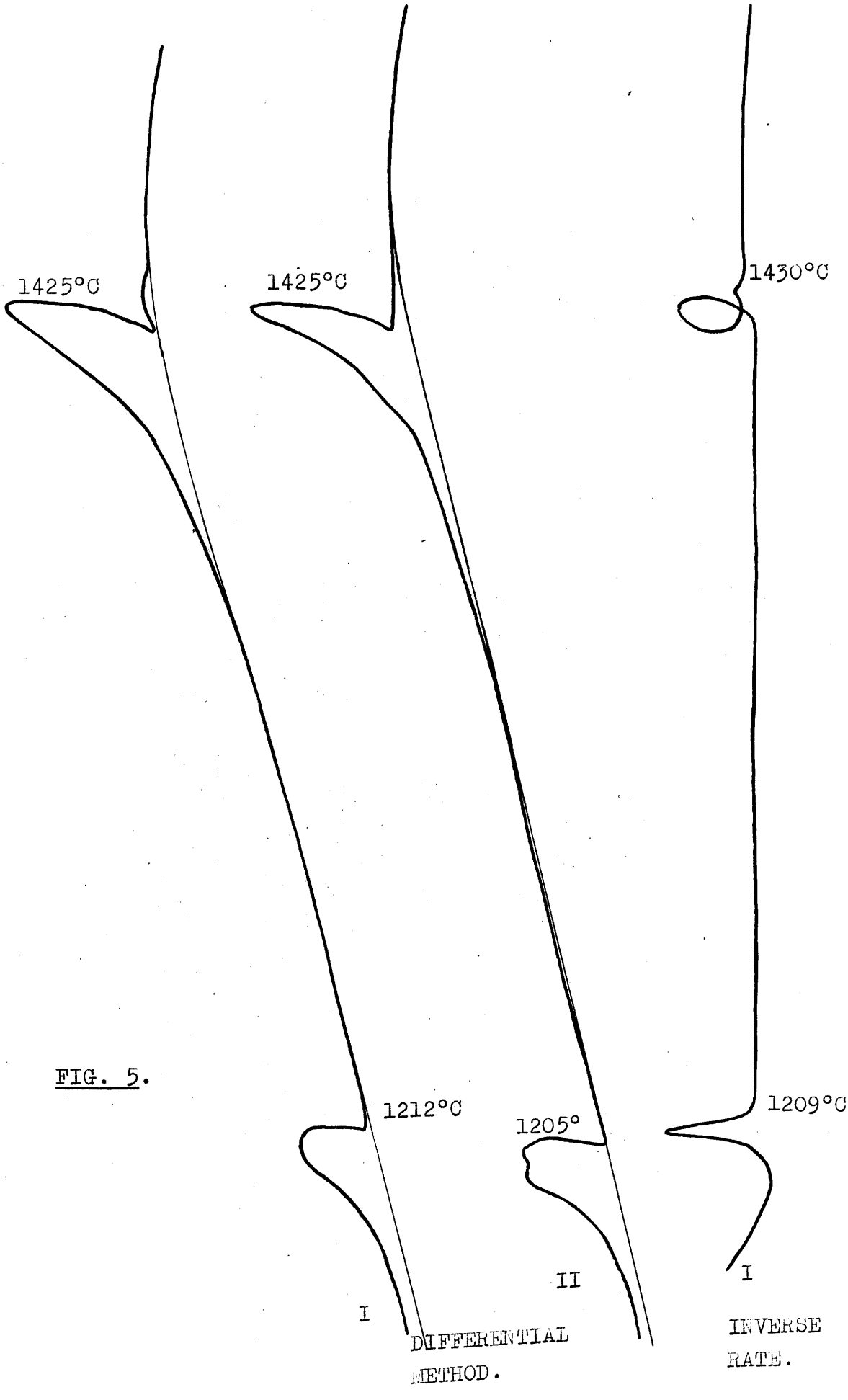


FIG. 5.

HEATING CURVES - DIFFERENTIAL METHOD.

CaO : 35.
Fe_2O_3 : 65.

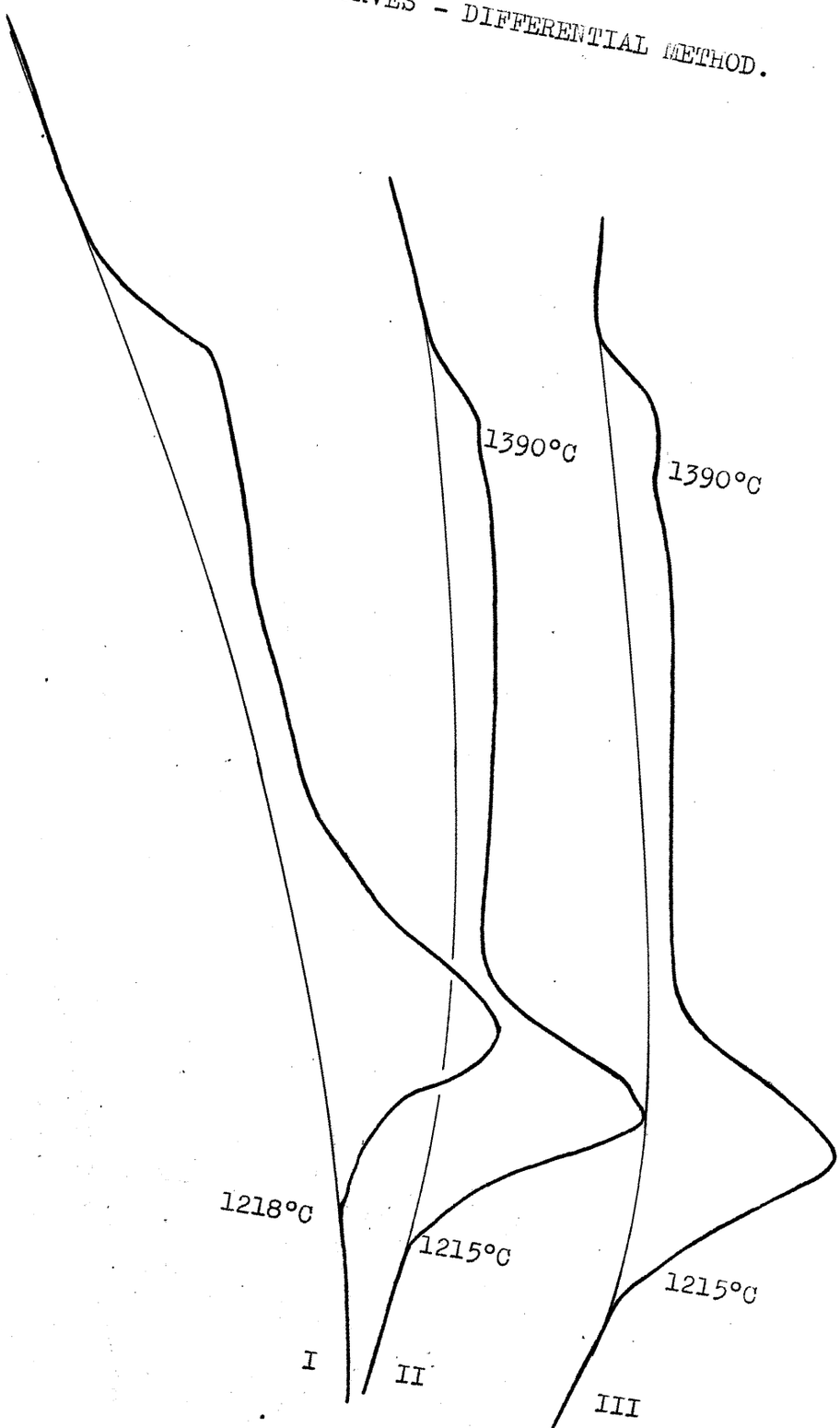


FIG. 6.

COOLING CURVES.

CaO : 35.

Fe_2O_3 : 65.

DIFFERENTIAL METHOD.

INVERSE RATE.

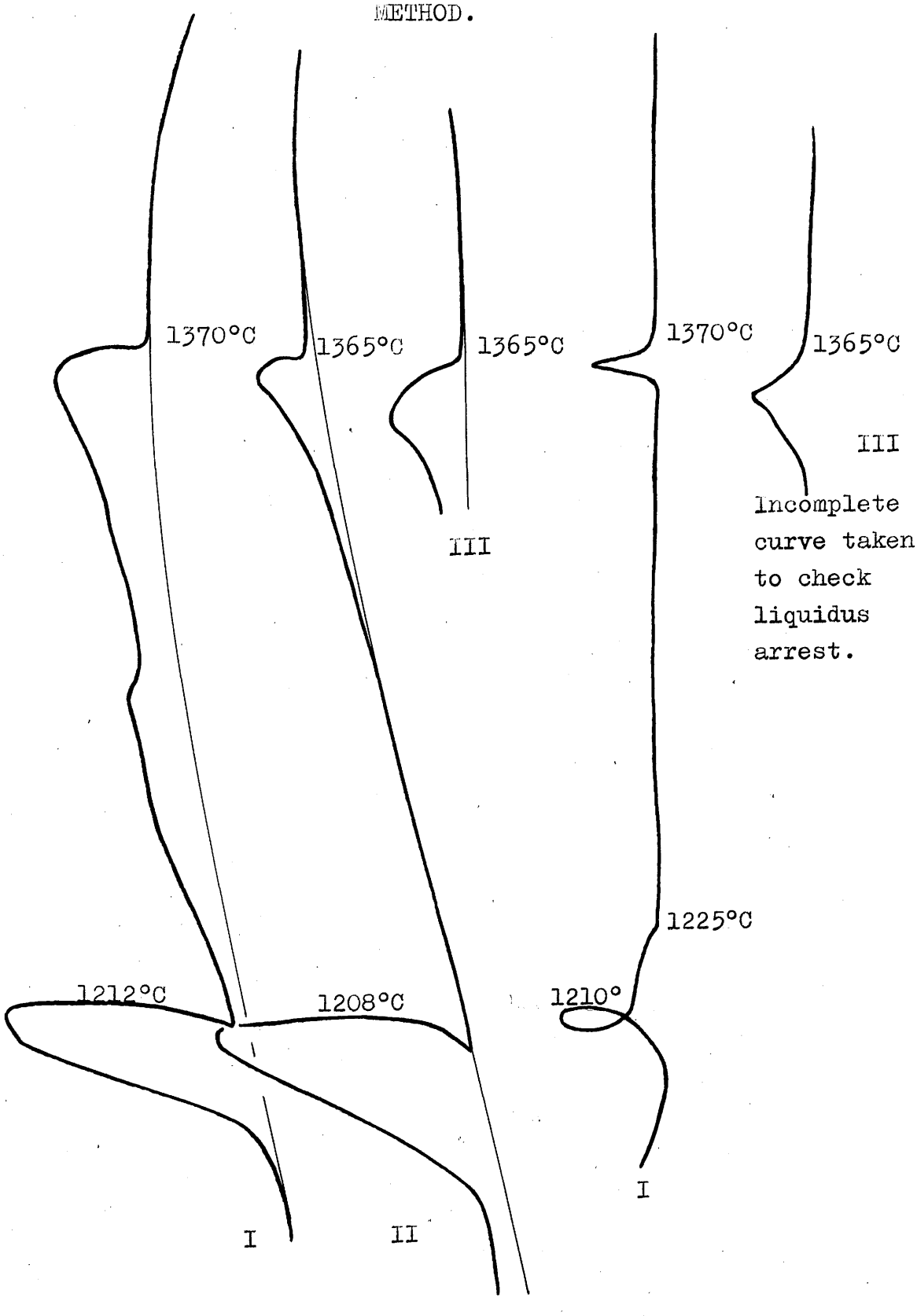
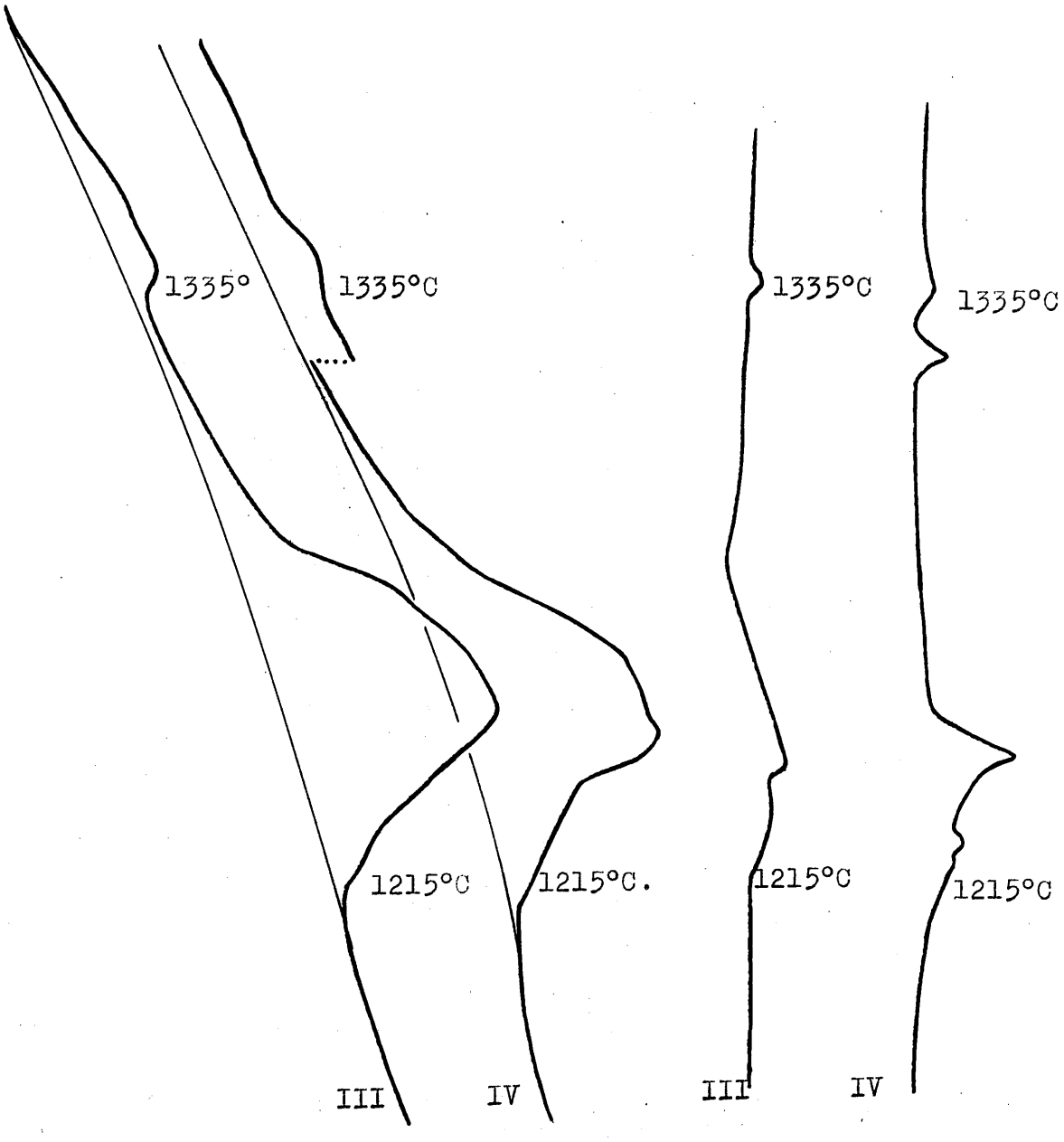


FIG. 7.

HEATING CURVES.

CaO : 30

Fe_2O_3 : 70.



DIFFERENTIAL METHOD. INVERSE RATE.

FIG. 8.

CaO : 30.

Fe_2O_3 : 70.

COOLING CURVES.

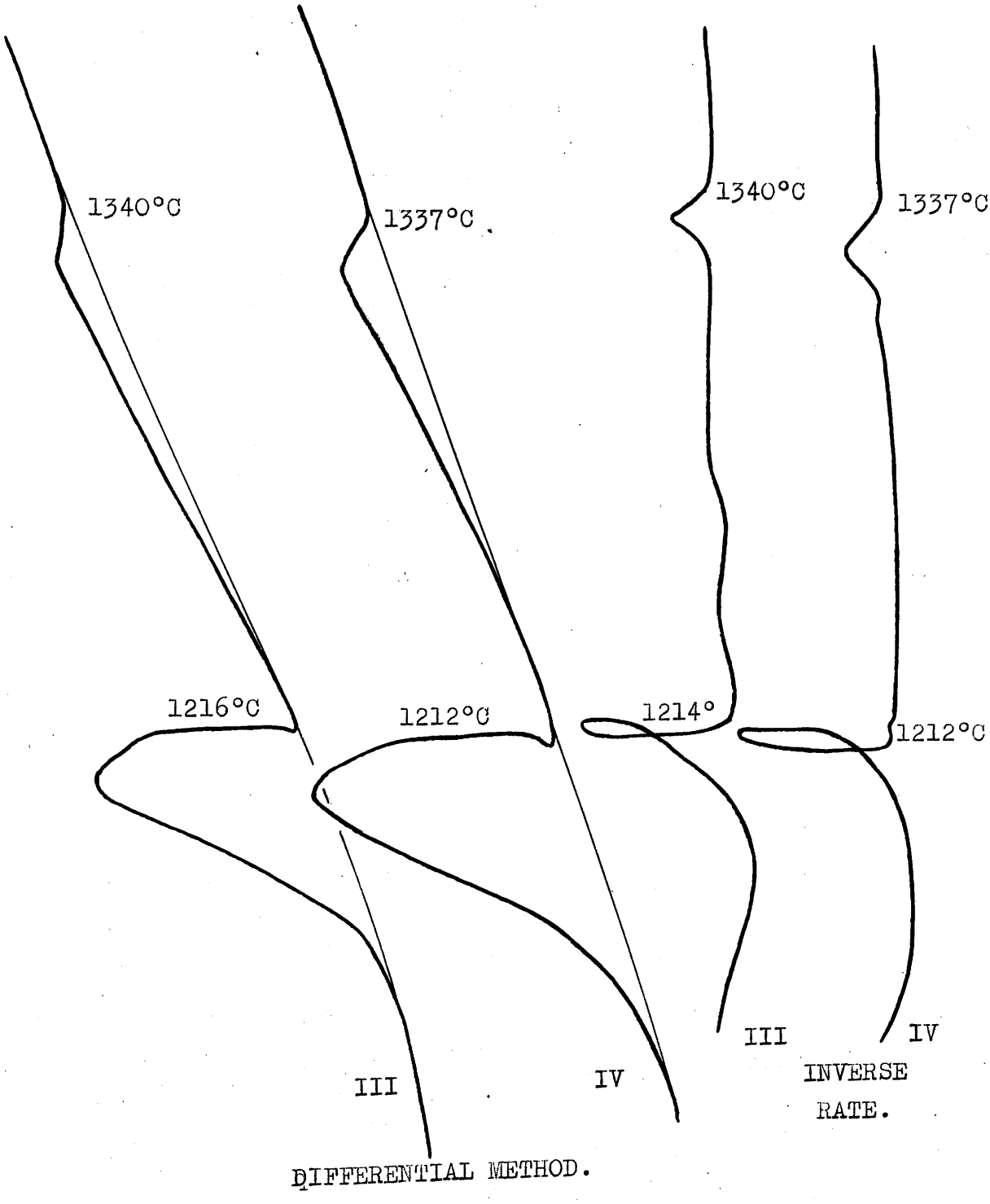


FIG. 9.

HEATING CURVES - DIFFERENTIAL METHOD.

CaO :27.5.
Fe_2O_3 :72.5.

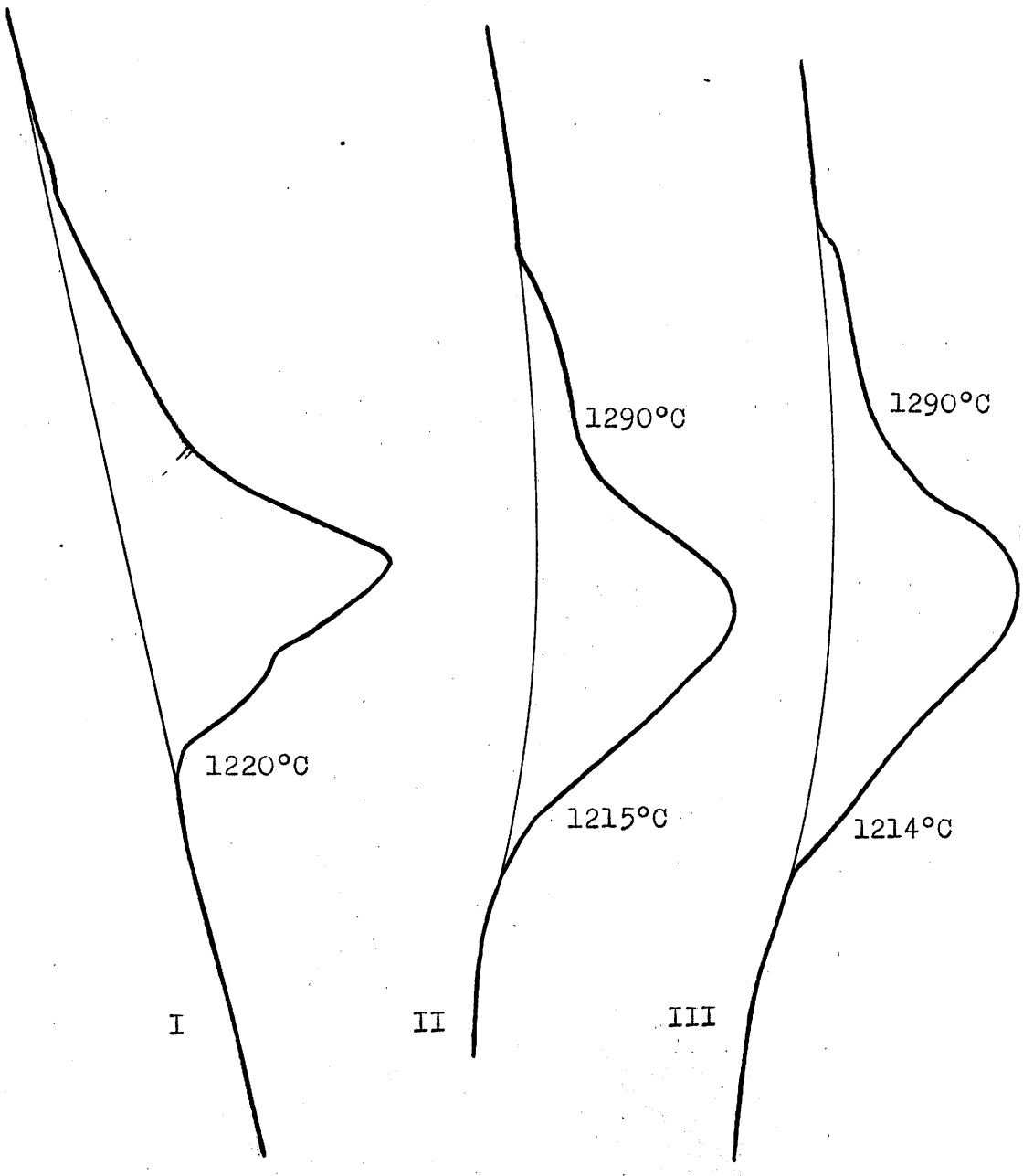


FIG. 10.

COOLING CURVES - DIFFERENTIAL METHOD.

CaO : 27.5.
Fe_2O_3 : 72.5.

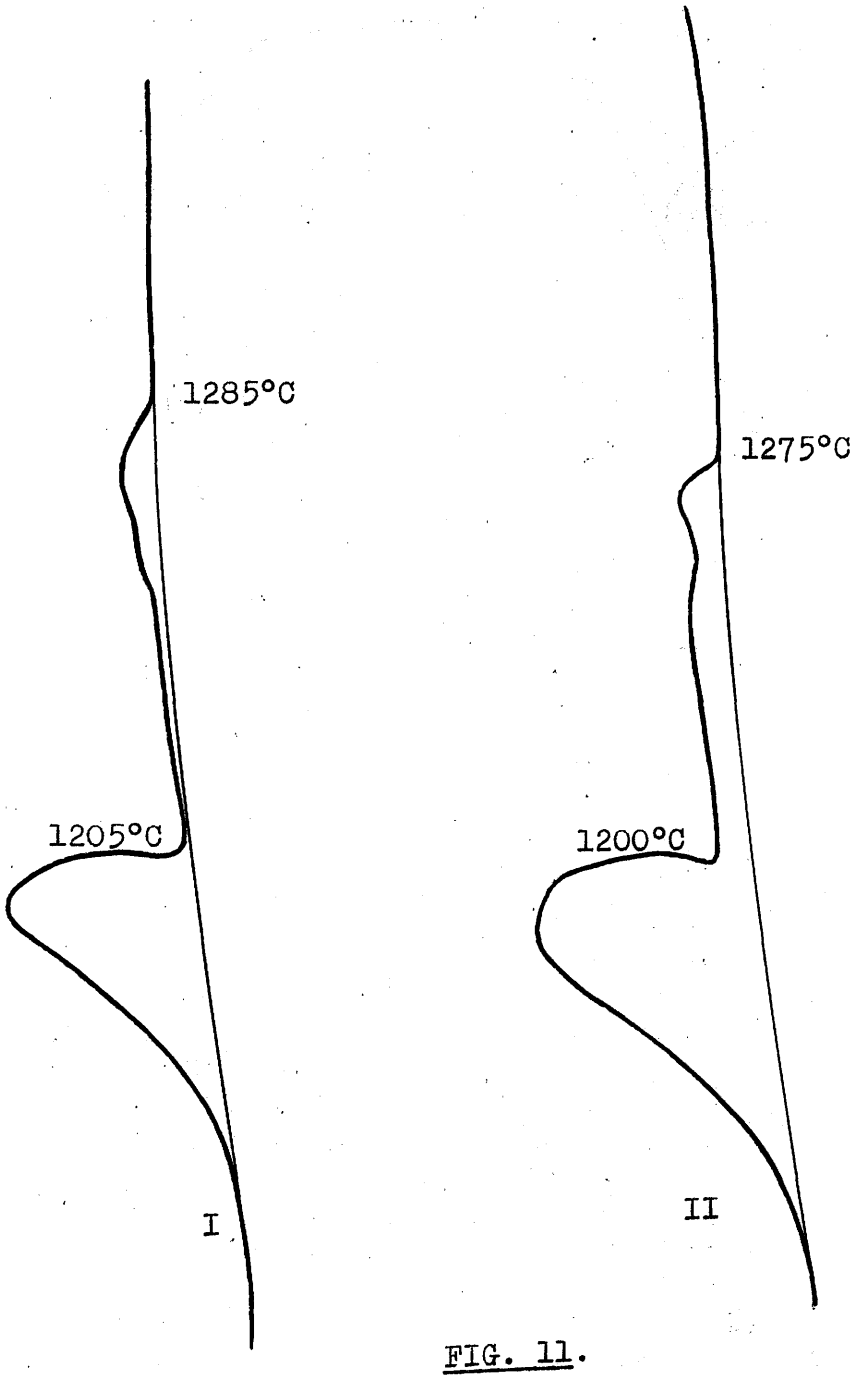
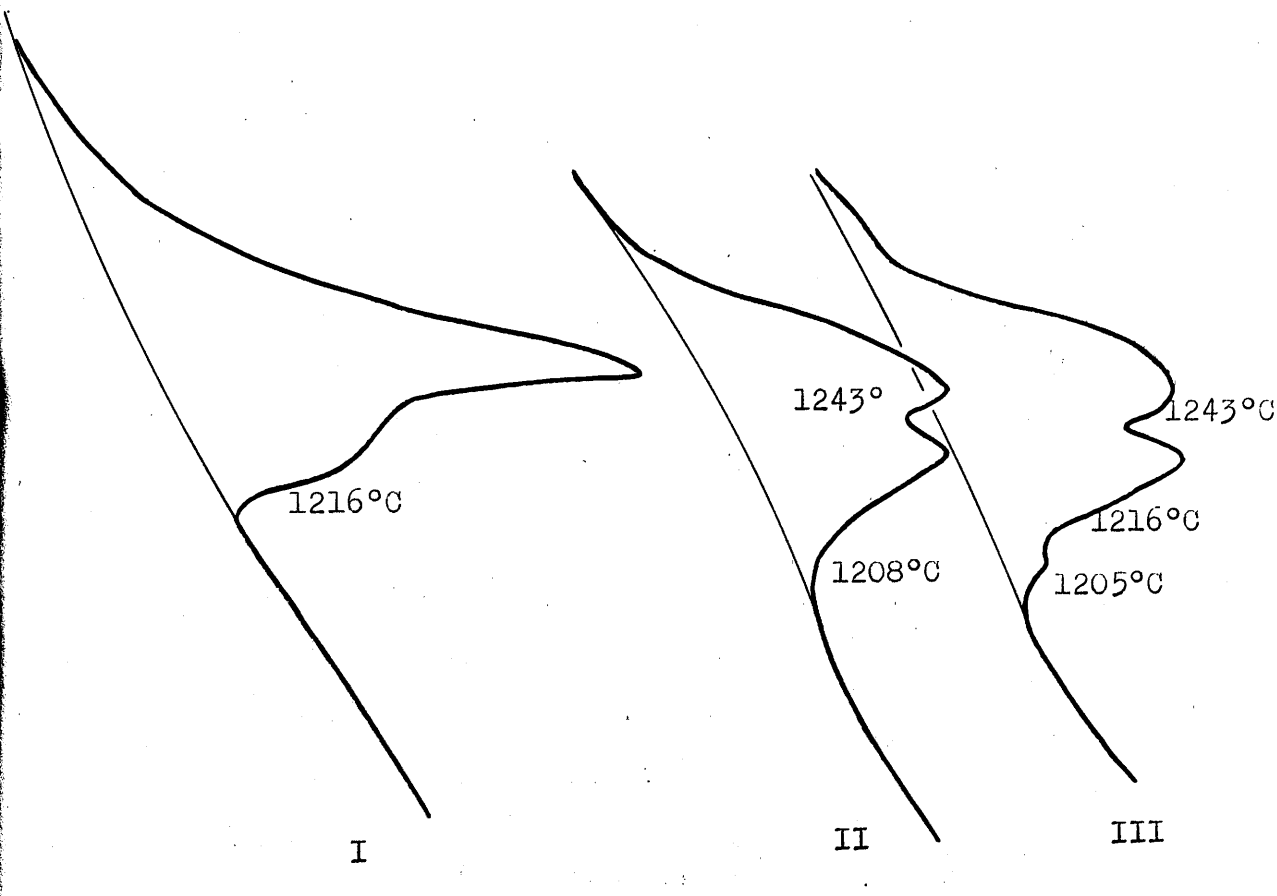


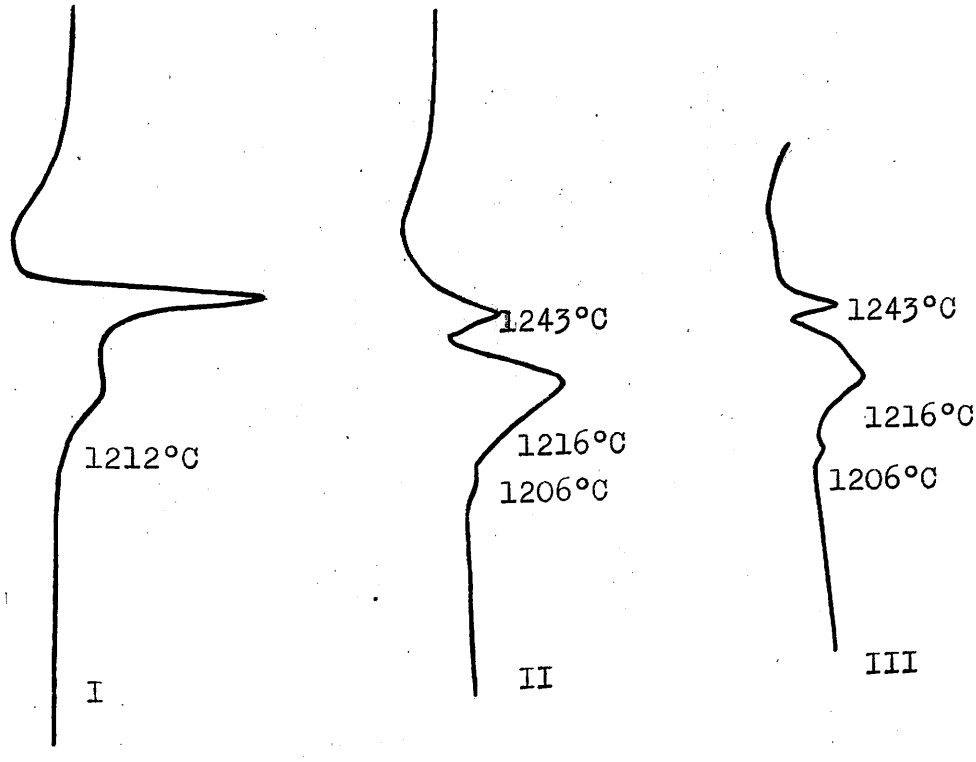
FIG. 11.

HEATING CURVES.

CaO : 25.9.
Fe_2O_3 : 74.1.
(Monocalcium ferrite)



DIFFERENTIAL METHOD.



INVERSE RATE.

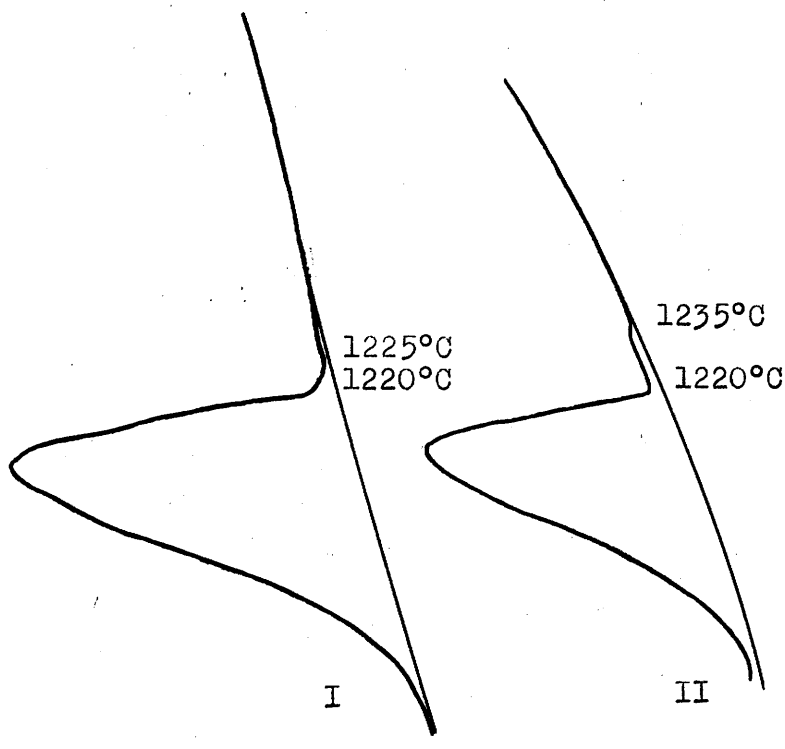
FIG. 12.

COOLING CURVES.

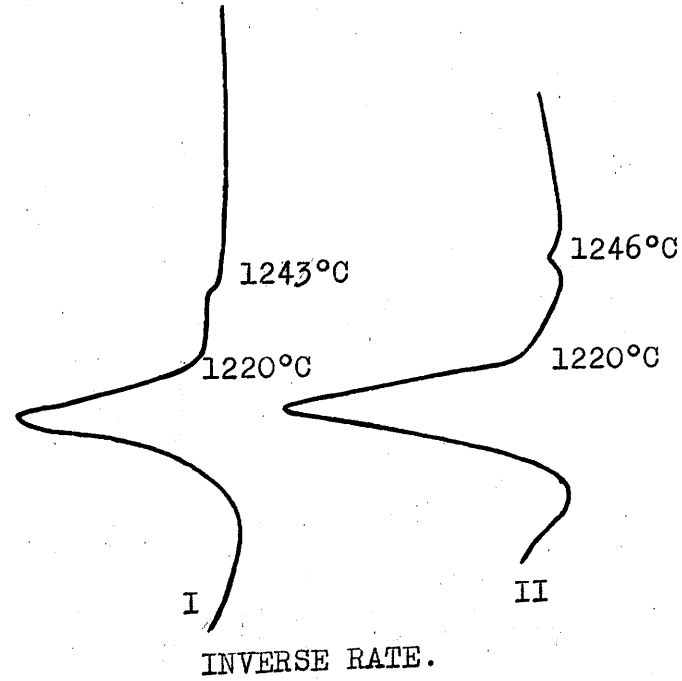
CaO : 25.9.

Fe_2O_3 : 74.1.

(Monocalcium ferrite)



DIFFERENTIAL METHOD.



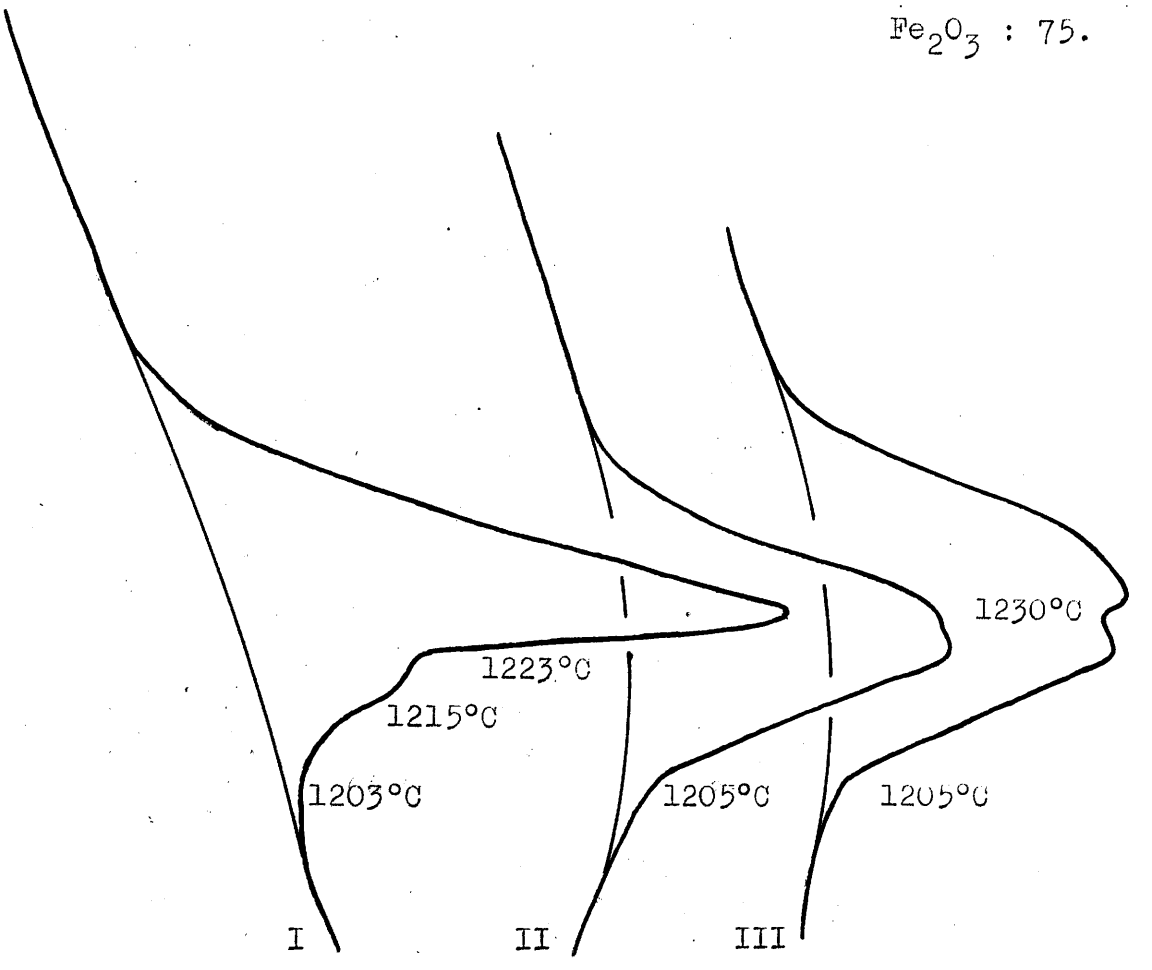
INVERSE RATE.

FIG. 13.

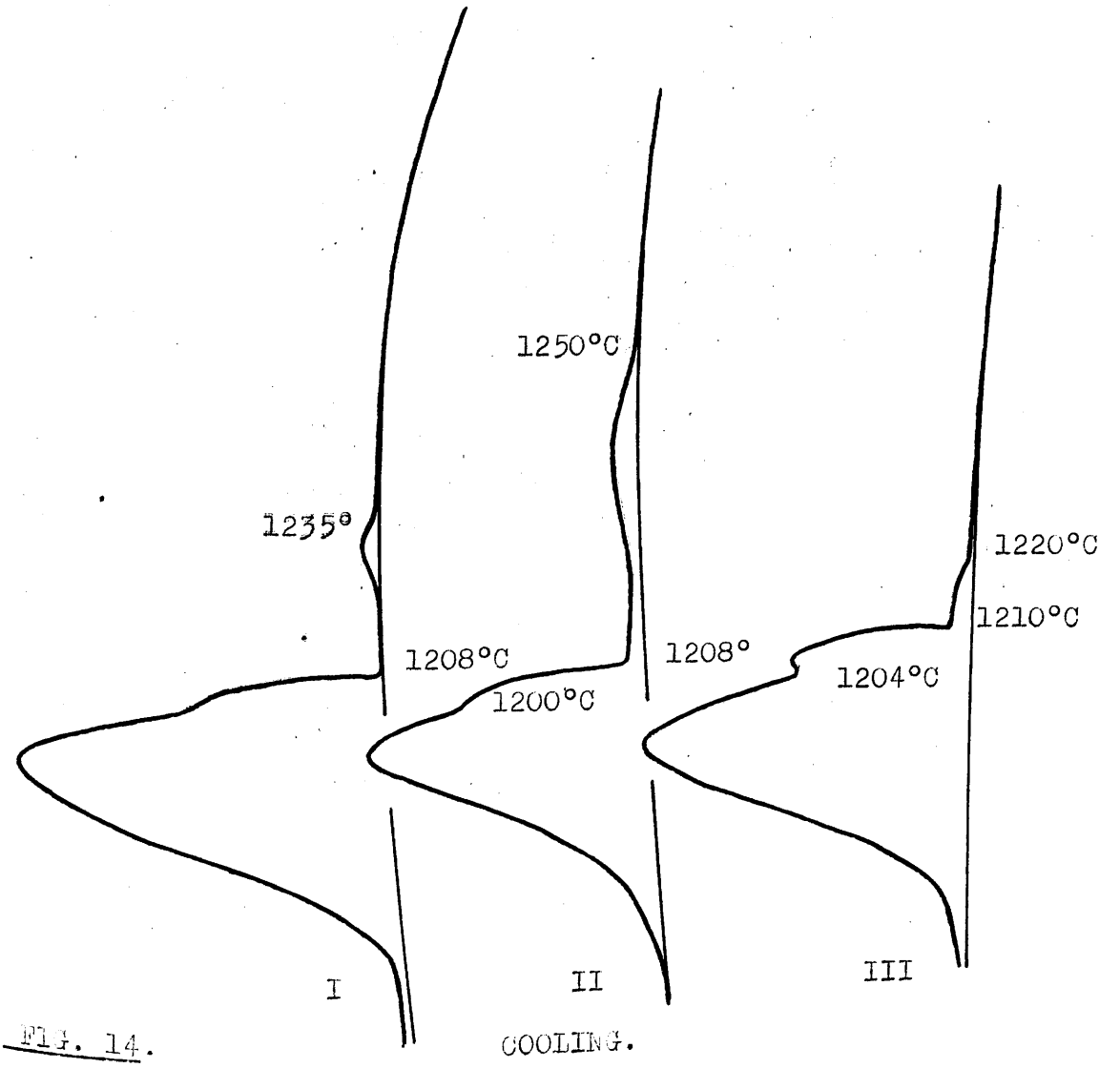
HEATING AND COOLING CURVES - DIFFERENTIAL METHOD.

CaO : 25.

Fe_2O_3 : 75.



HEATING.



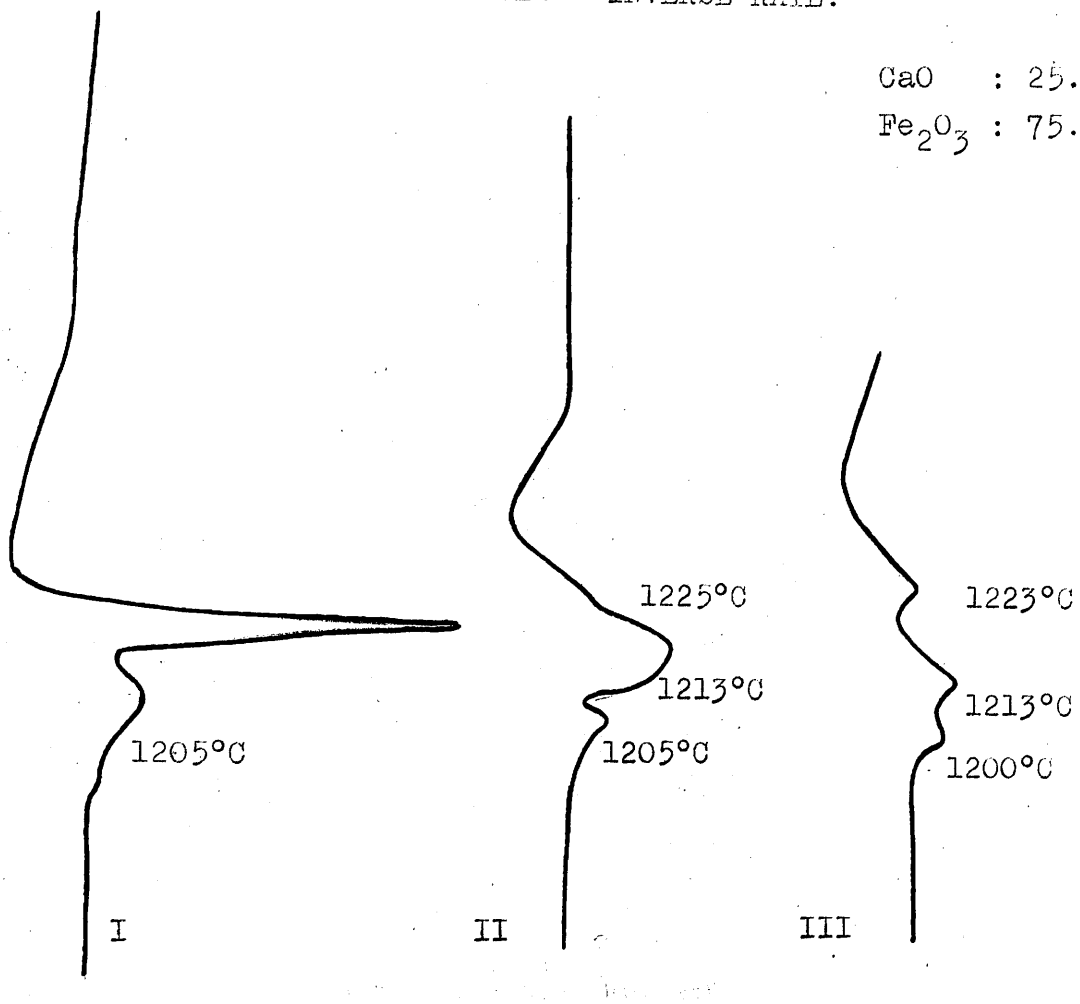
COOLING.

Fig. 14.

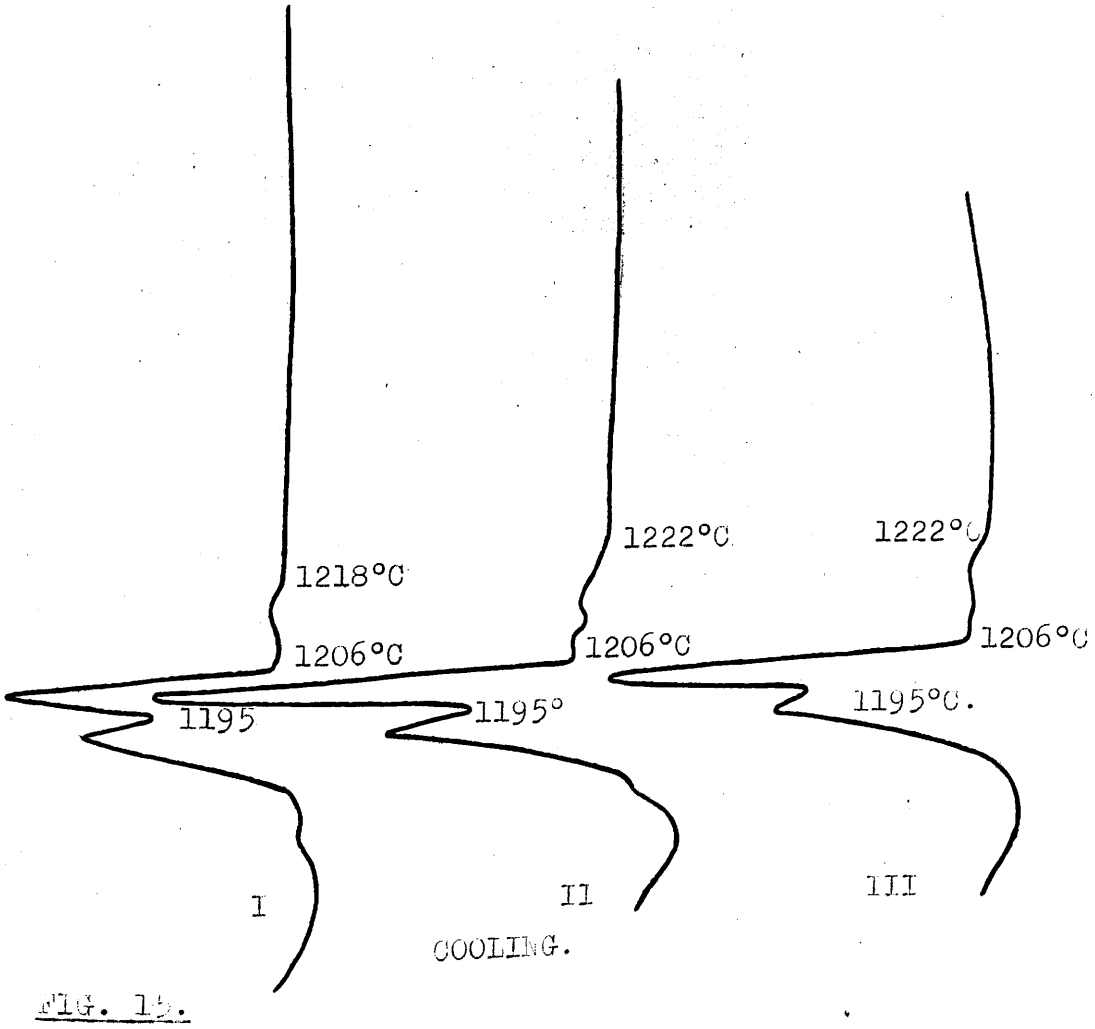
HEATING AND COOLING CURVES - INVERSE RATE.

CaO : 25.

Fe_2O_3 : 75.



HEATING.



COOLING.

FIG. 15.

HEATING AND COOLING CURVES.

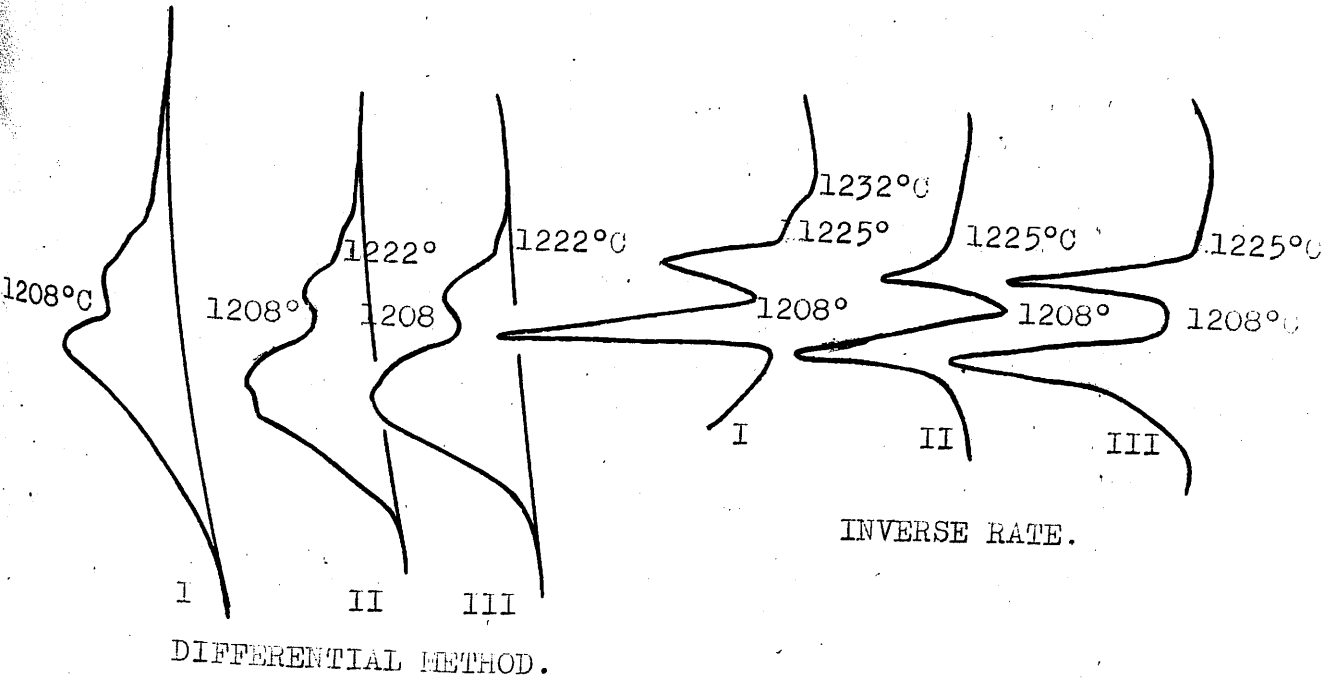
CaO : 22.5.

Fe_2O_3: 77.5.

DIFFERENTIAL METHOD?

INVERSE RATE.

HEATING.



DIFFERENTIAL METHOD.

INVERSE RATE.

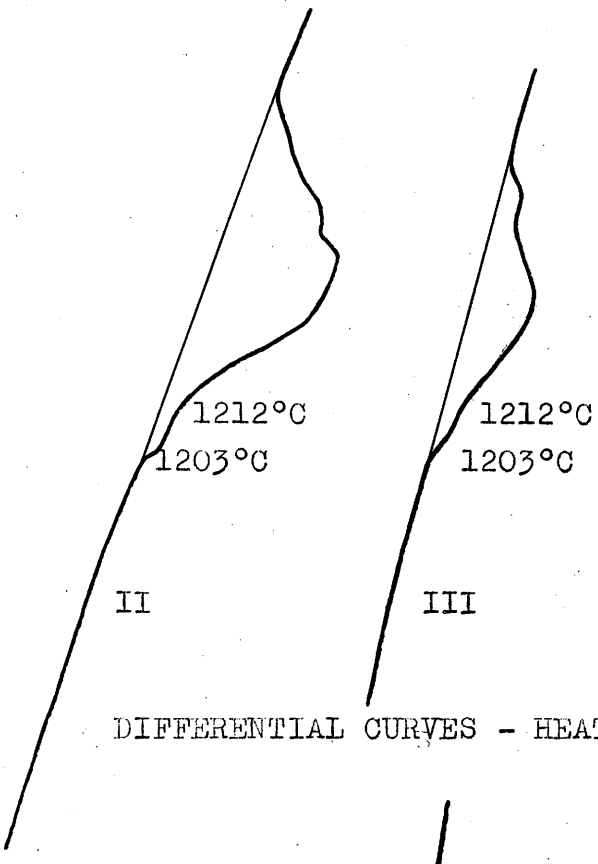
COOLING.

FIG. 16.

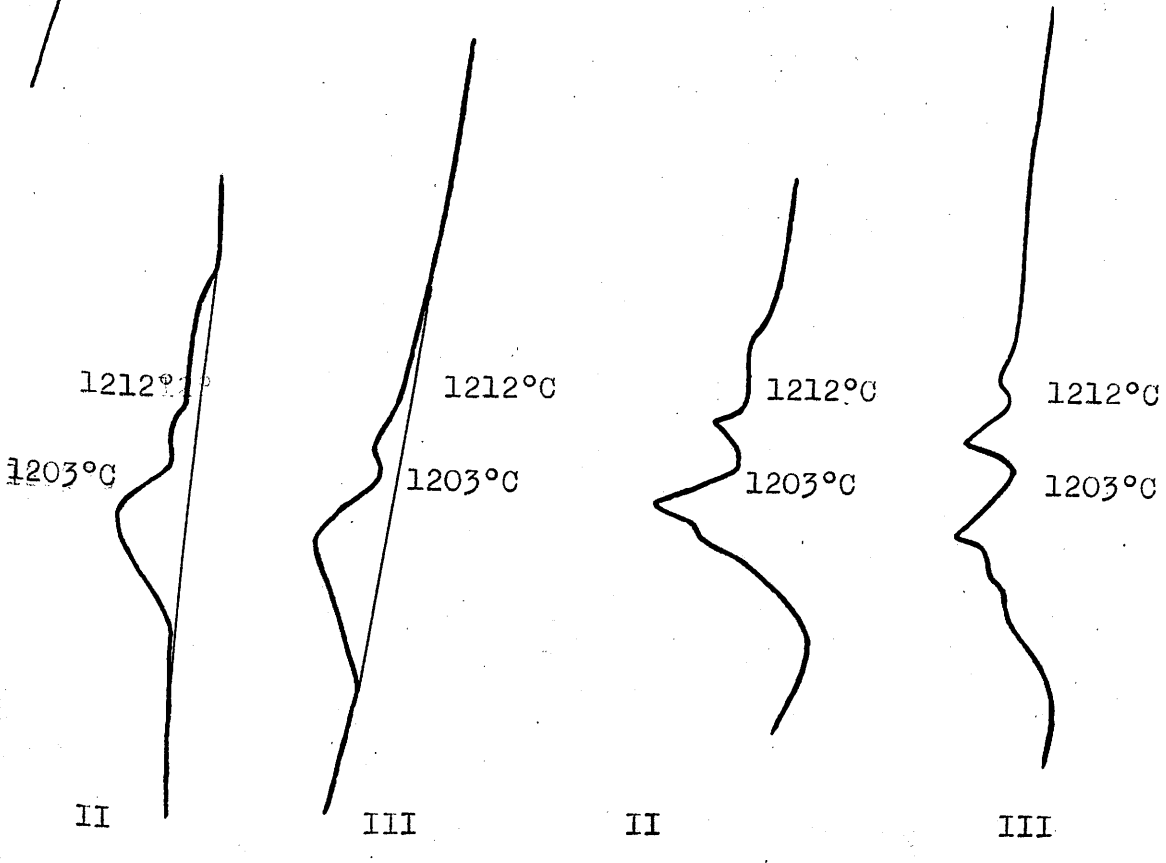
HEATING AND COOLING CURVES.

CaO : 20.

Fe_2O_3 : 80.



DIFFERENTIAL CURVES - HEATING.



DIFFERENTIAL METHOD.

INVERSE RATE.

COOLING.

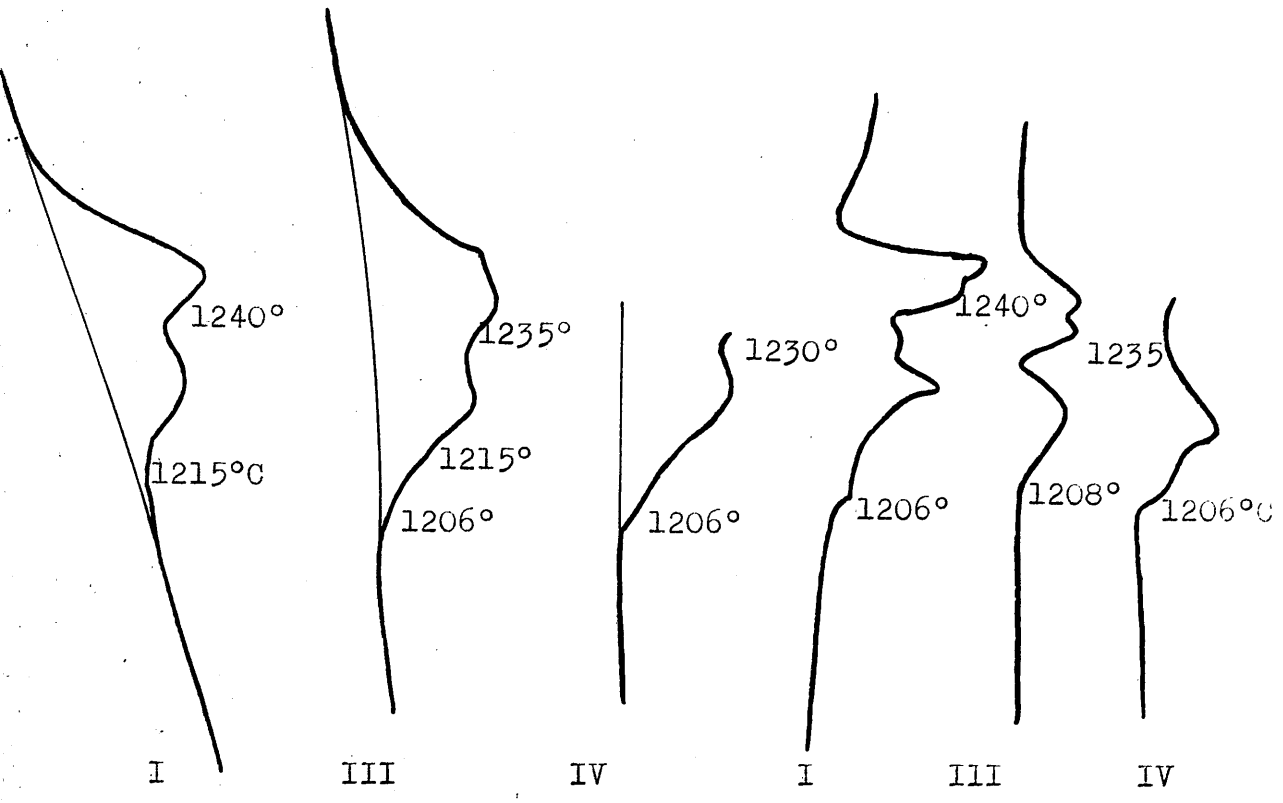
FIG. 17.

HEATING AND COOLING CURVES.

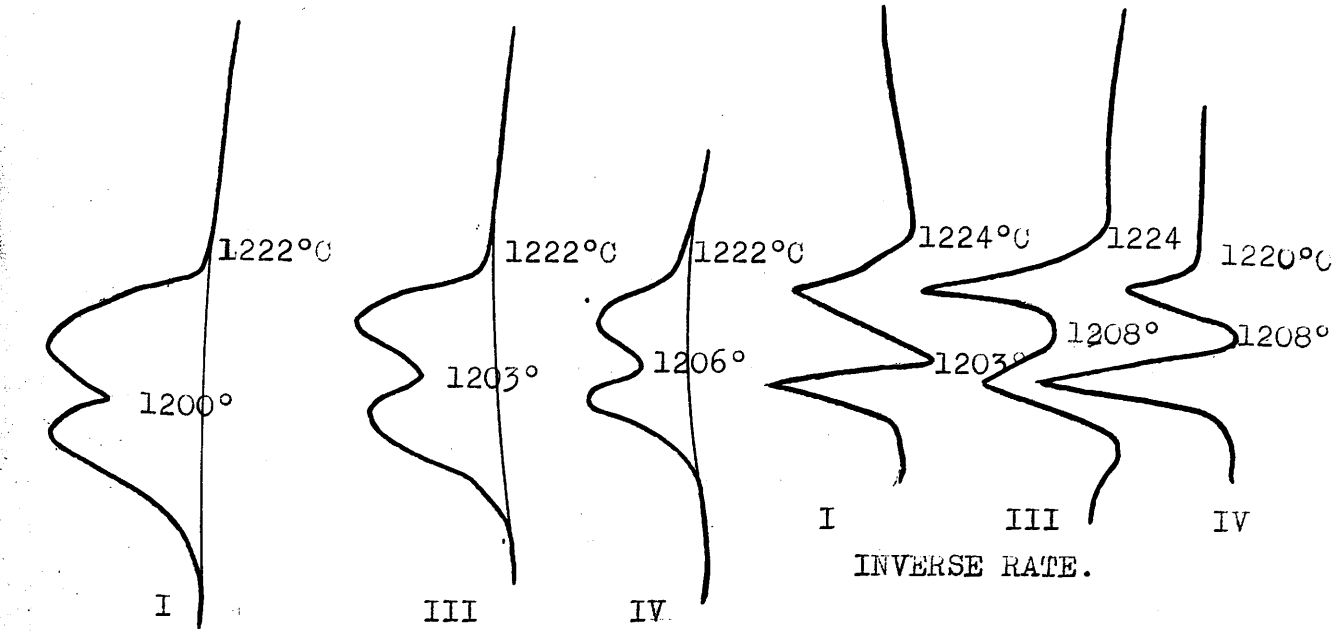
CaO : 17.5

Fe_2O_3 : 82.5.

HEATING CURVES.



DIFFERENTIAL METHOD. INVERSE RATE.



DIFFERENTIAL METHOD. INVERSE RATE.

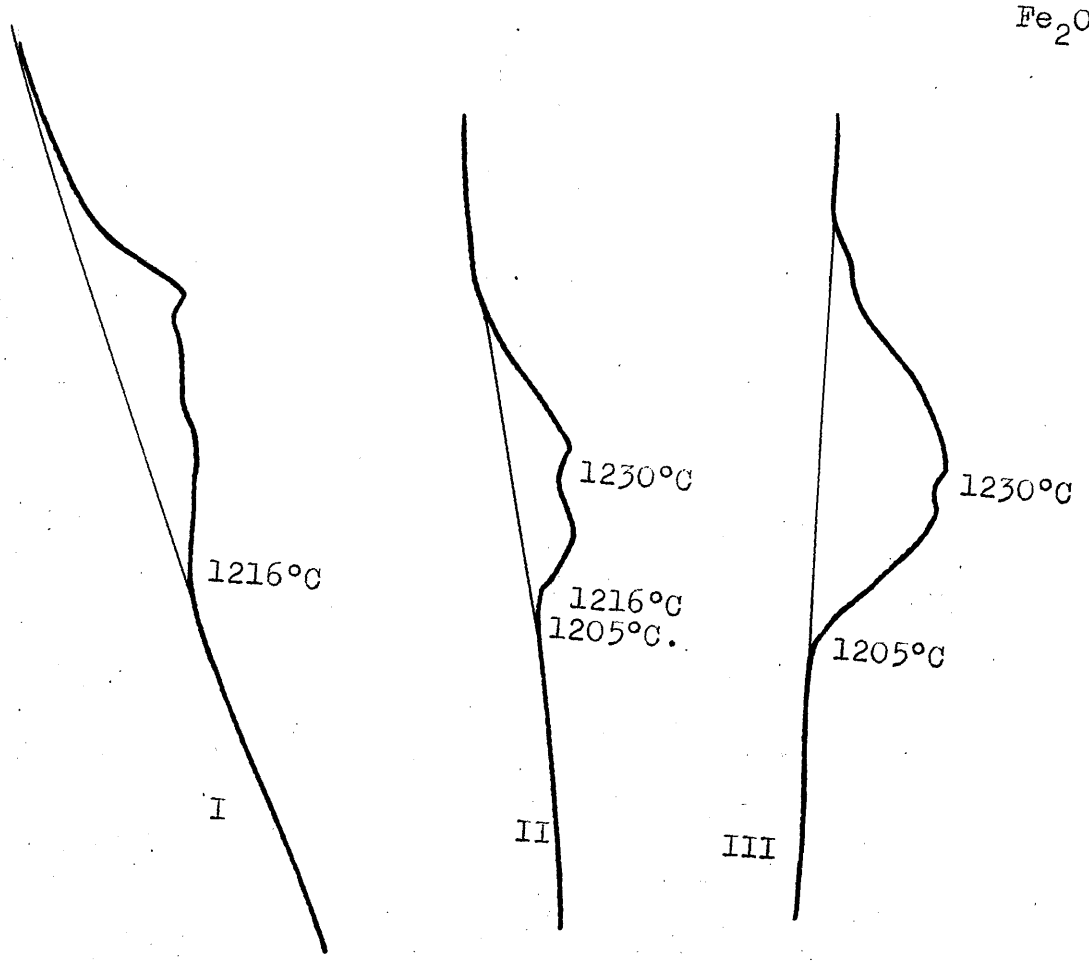
COOLING.

FIG. 18.

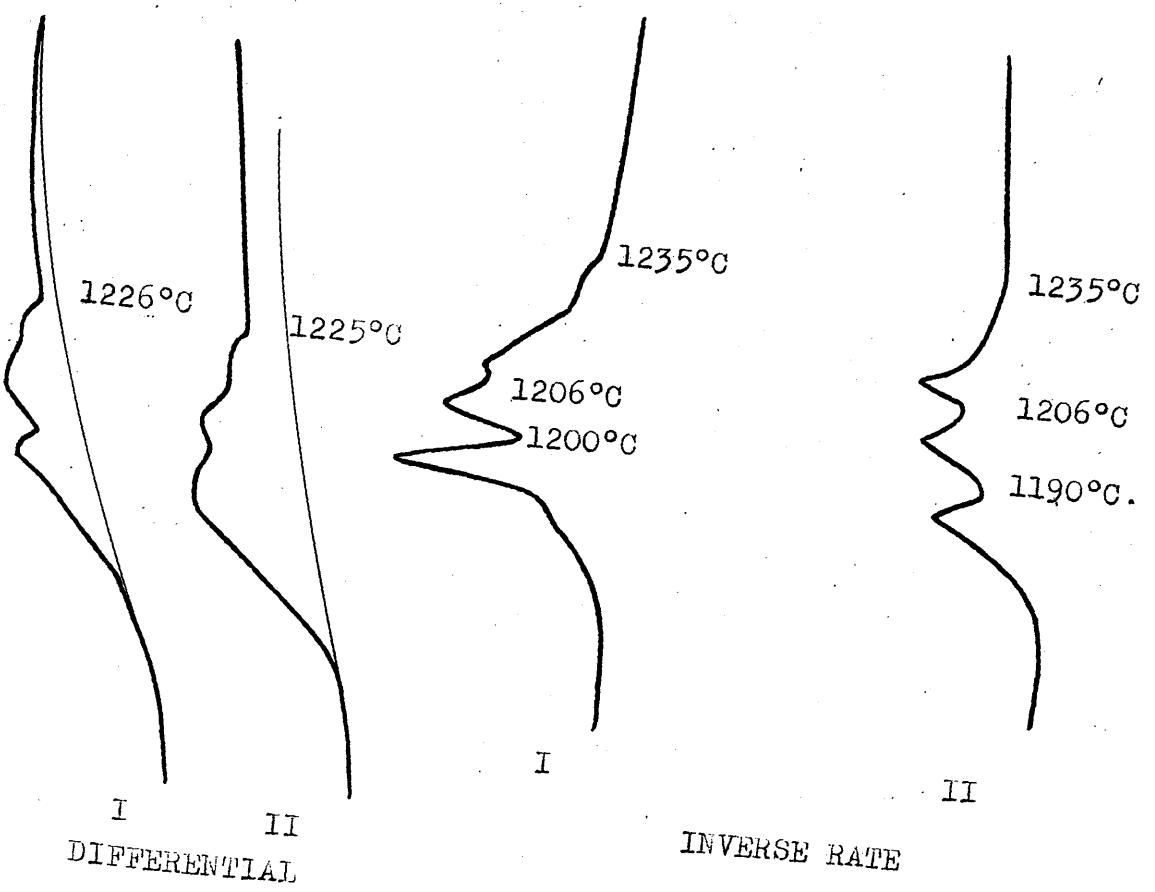
HEATING AND COOLING CURVES.

CaO : 15.

Fe_2O_3 : 85.



DIFFERENTIAL CURVES - HEATING.

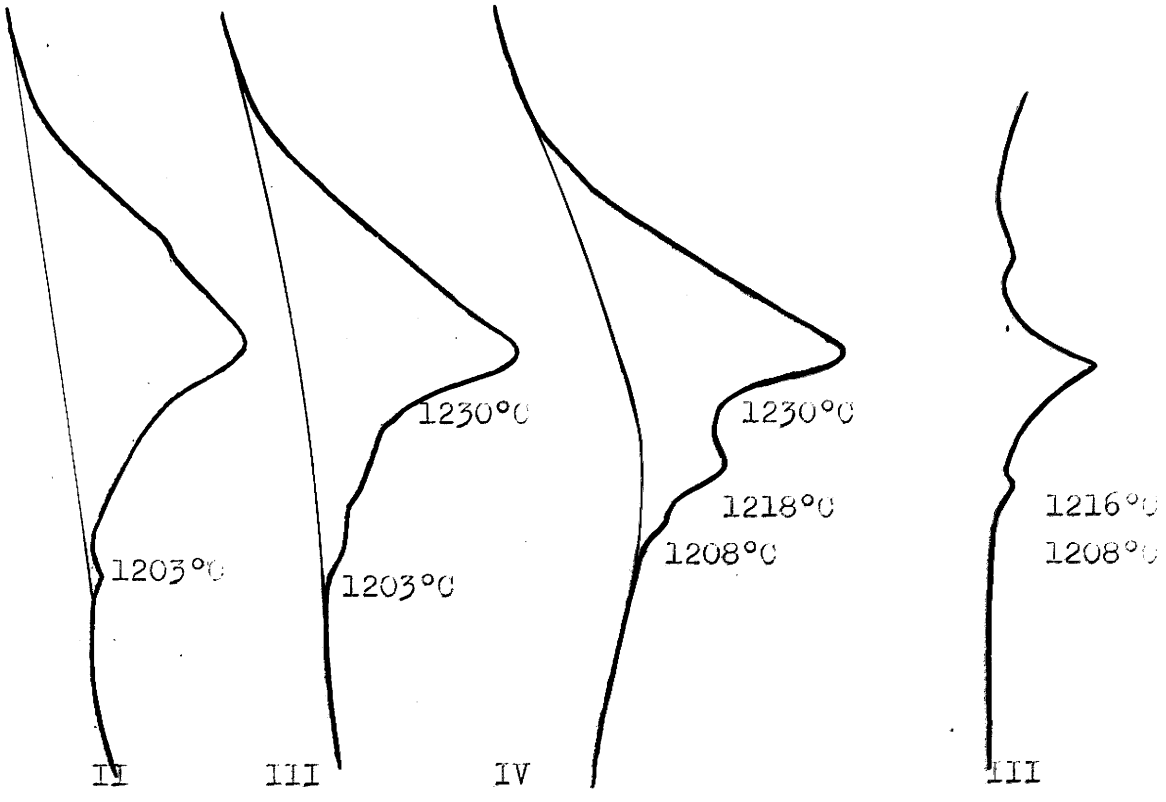


COOLING.

FIG. 19.

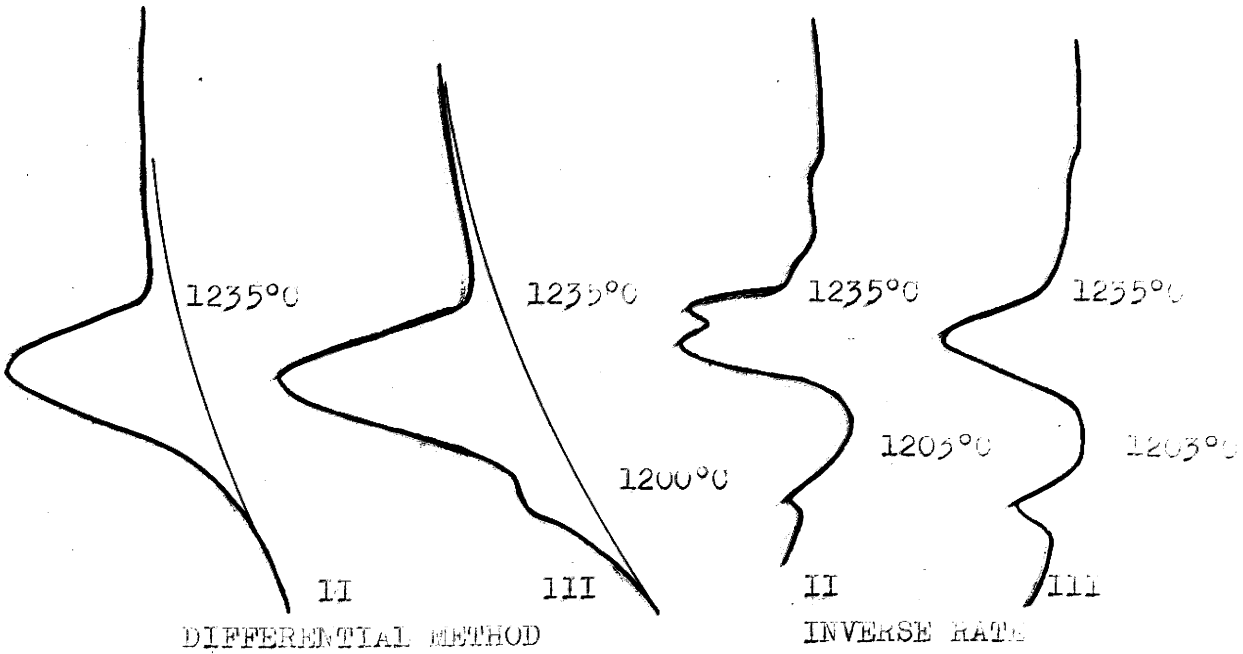
CaO : 12.

Fe_2O_3 : 88.



DIFFERENTIAL METHOD. INVERSE RATE.

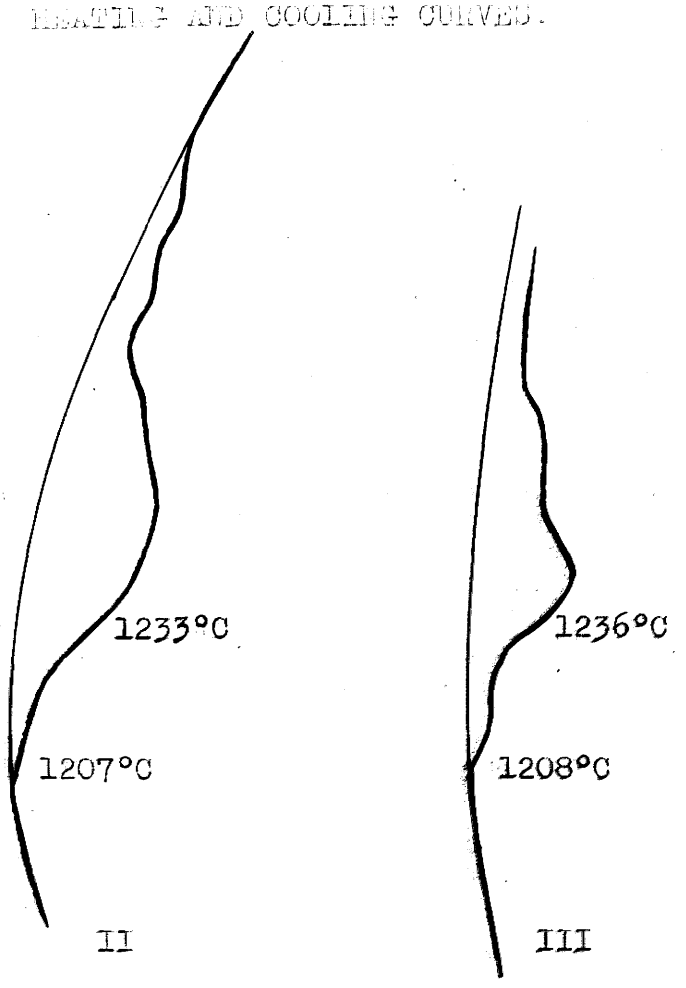
HEATING CURVES.



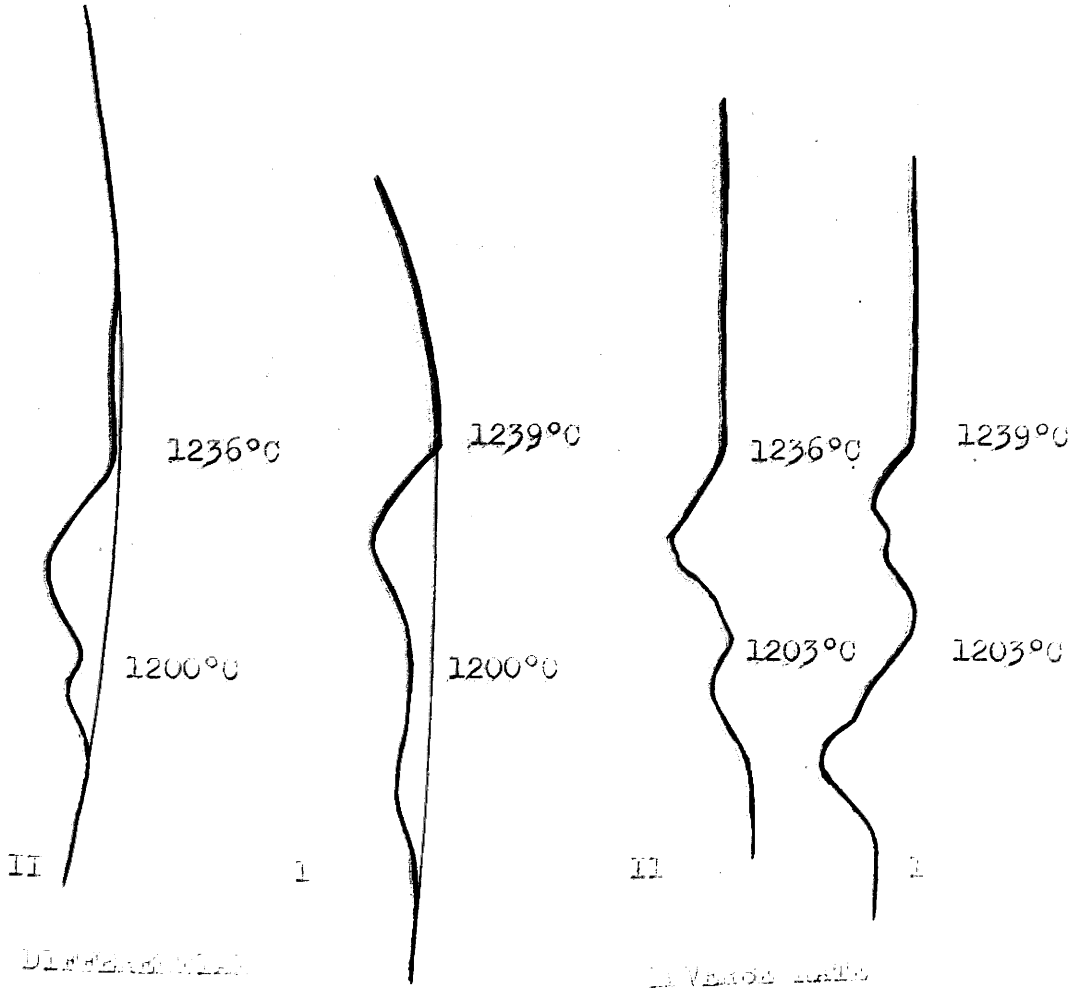
DIFFERENTIAL METHOD INVERSE RATE

COOLING CURVES.

FIG. 20.



HEATING CURVES - DIFFERENTIAL METHOD.



HEATING CURVES - DIFFERENTIAL METHOD.

CaO : 7.5.
Fe_2O_3 : 92.5

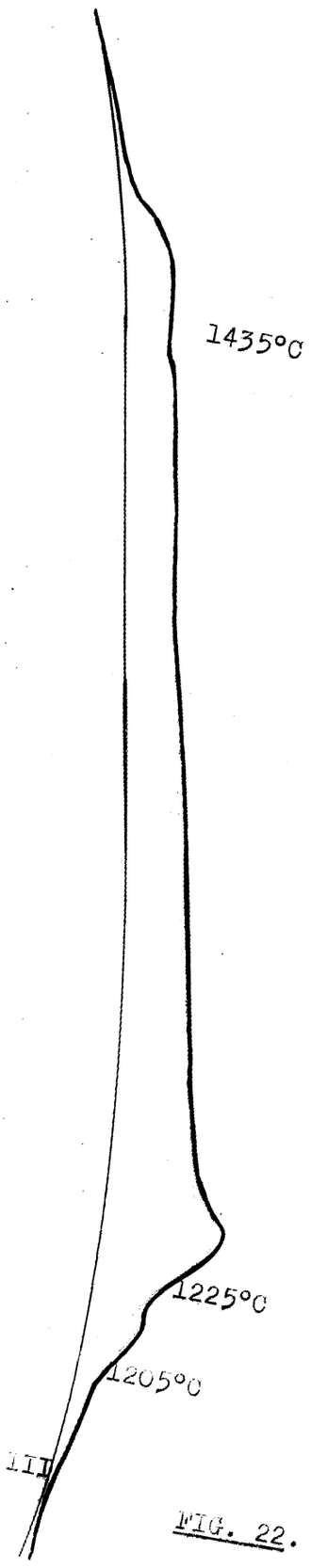
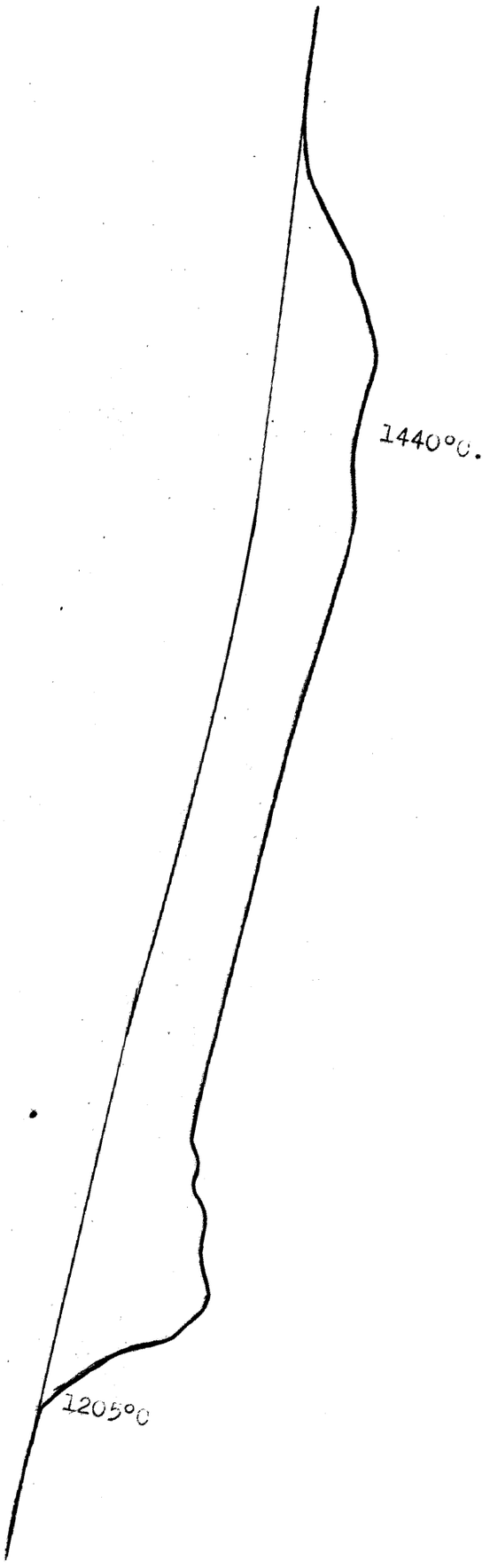
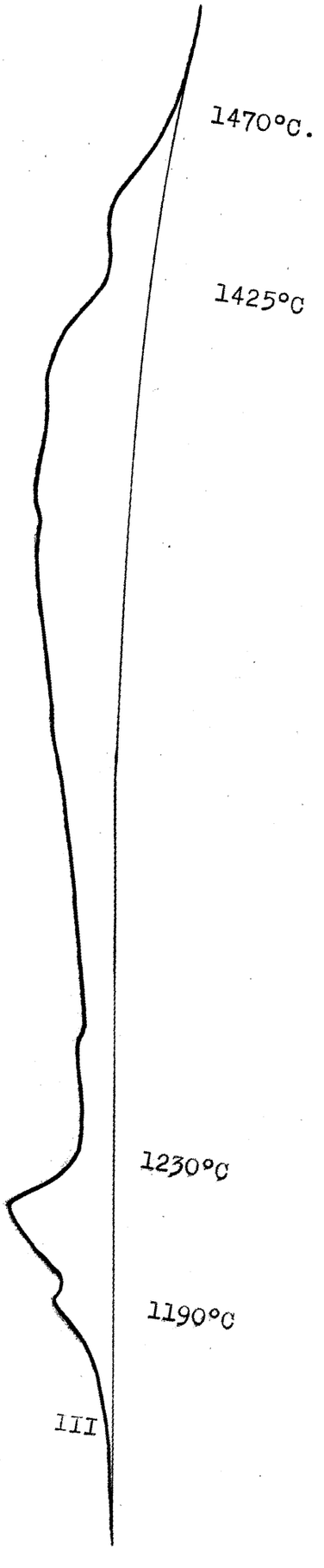


FIG. 22.



COOLING CURVES - DIFFERENTIAL METHOD.

CaO 47.5
Fe_2O_3 52.5



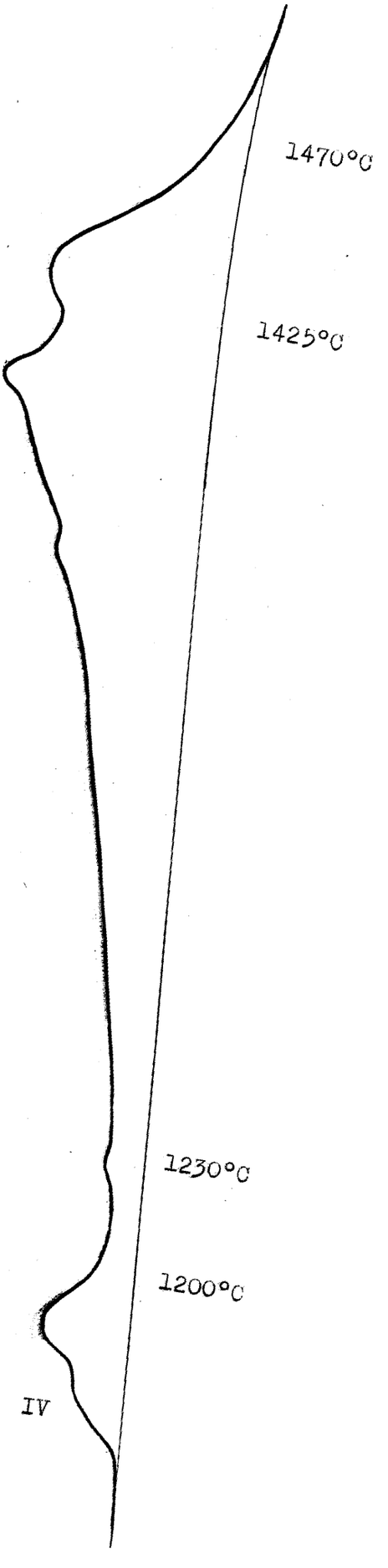


FIG. 22.

HEATING CURVES - DIFFERENTIAL METHOD.

CaO : 5.
Fe_2O_3 : 95.

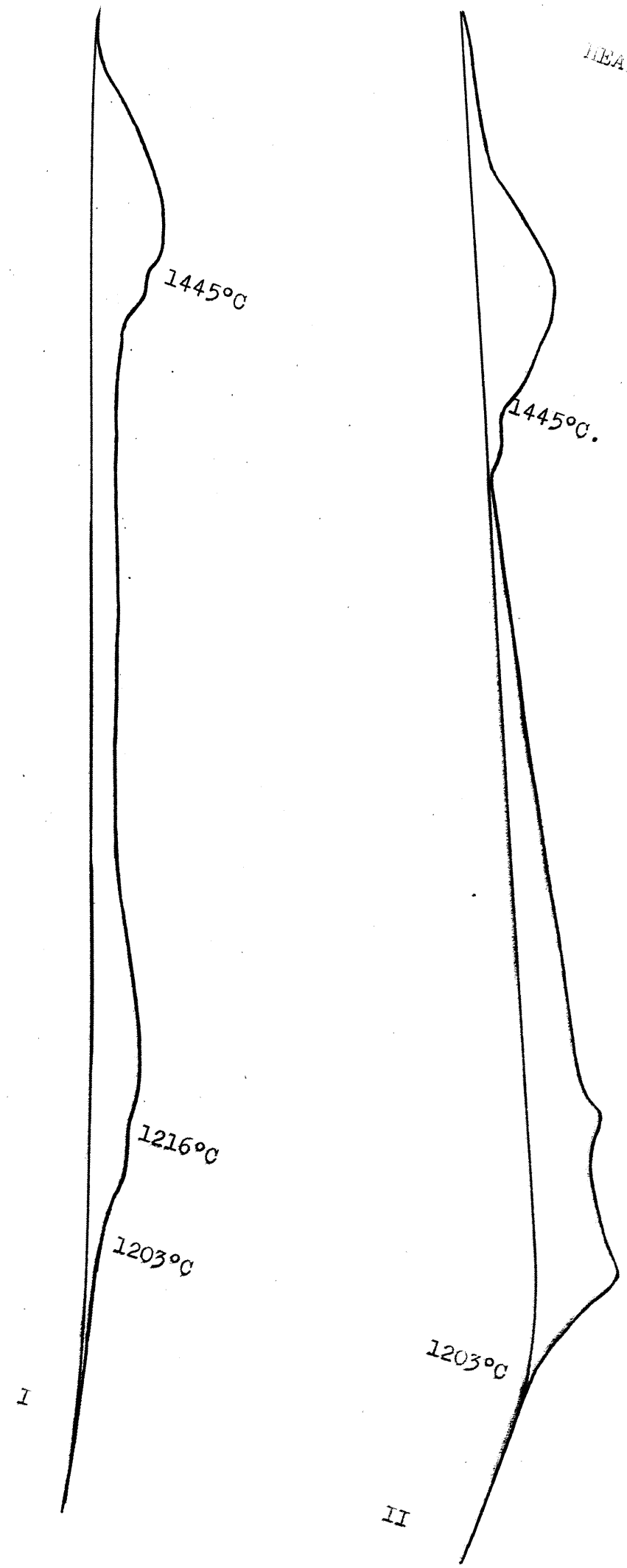


FIG. 24.

COOLING CURVES - DIFFERENTIAL METHOD.

CaO : 5

Fe_2O_3 : 95.

FIG. 25.

Fe_2O_3

HEATING CURVE - DIFFERENTIAL METHOD.

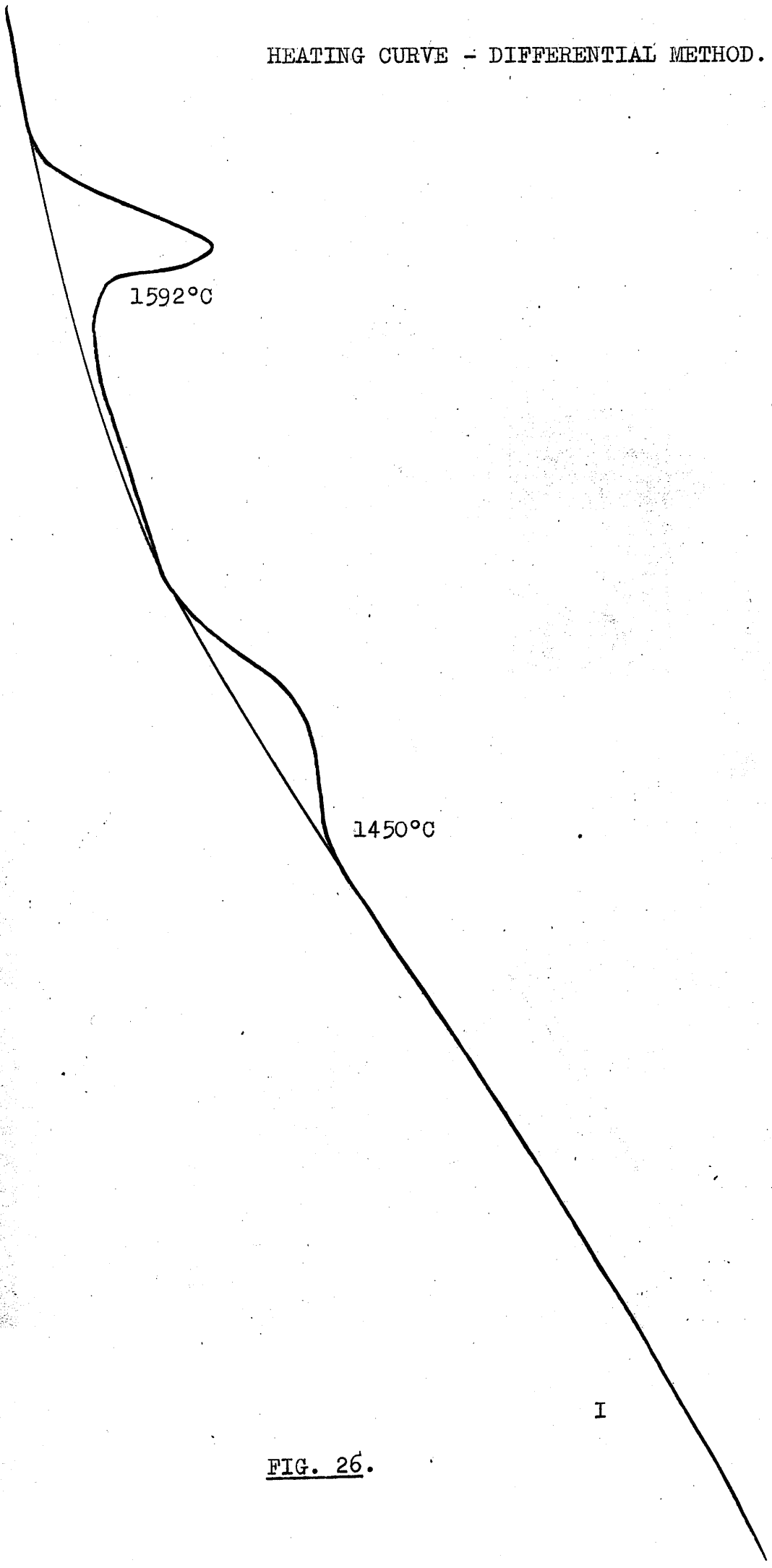


FIG. 26.

Fe_2O_3

COOLING CURVE - DIFFERENTIAL METHOD.

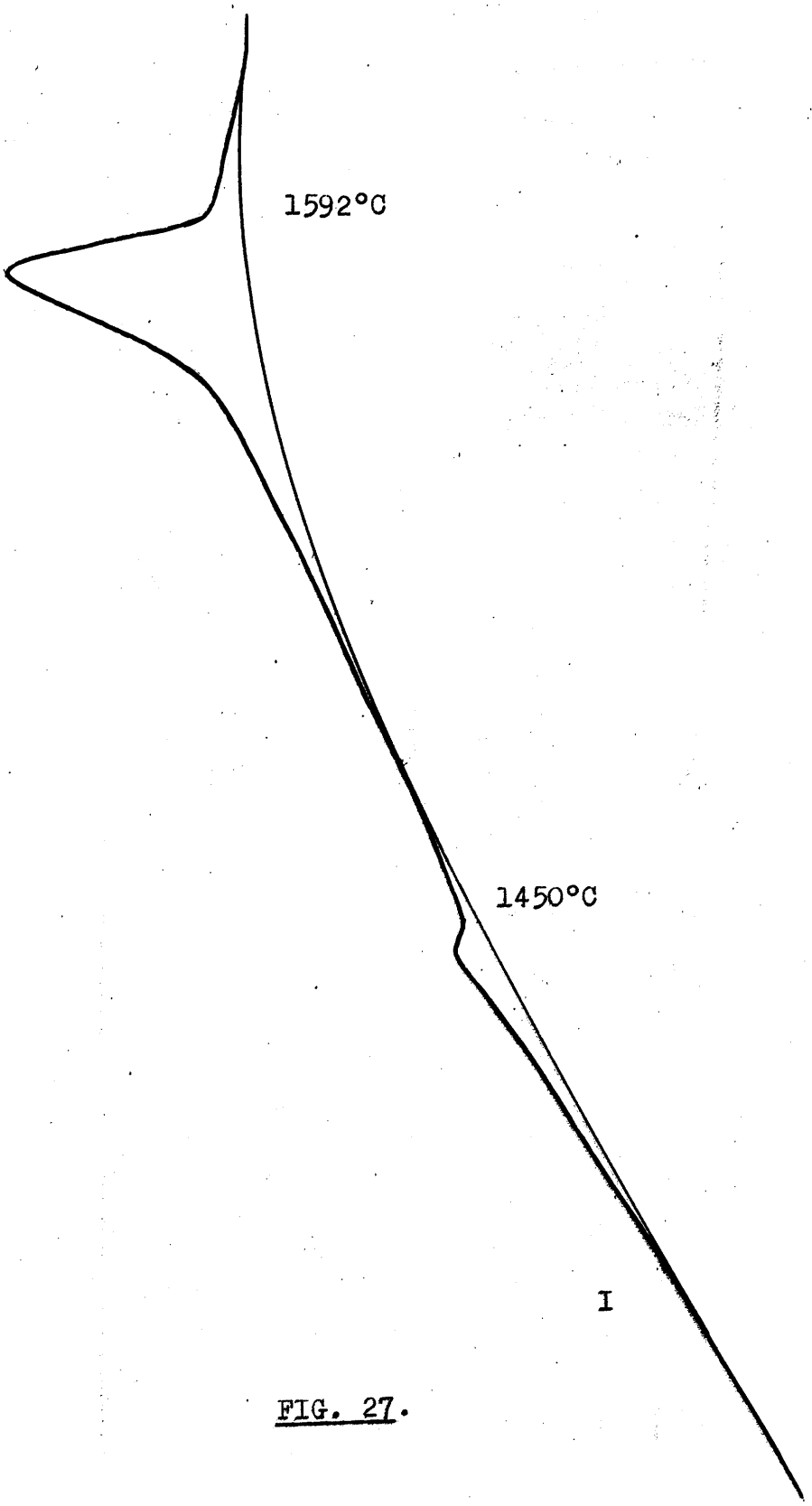


FIG. 27.

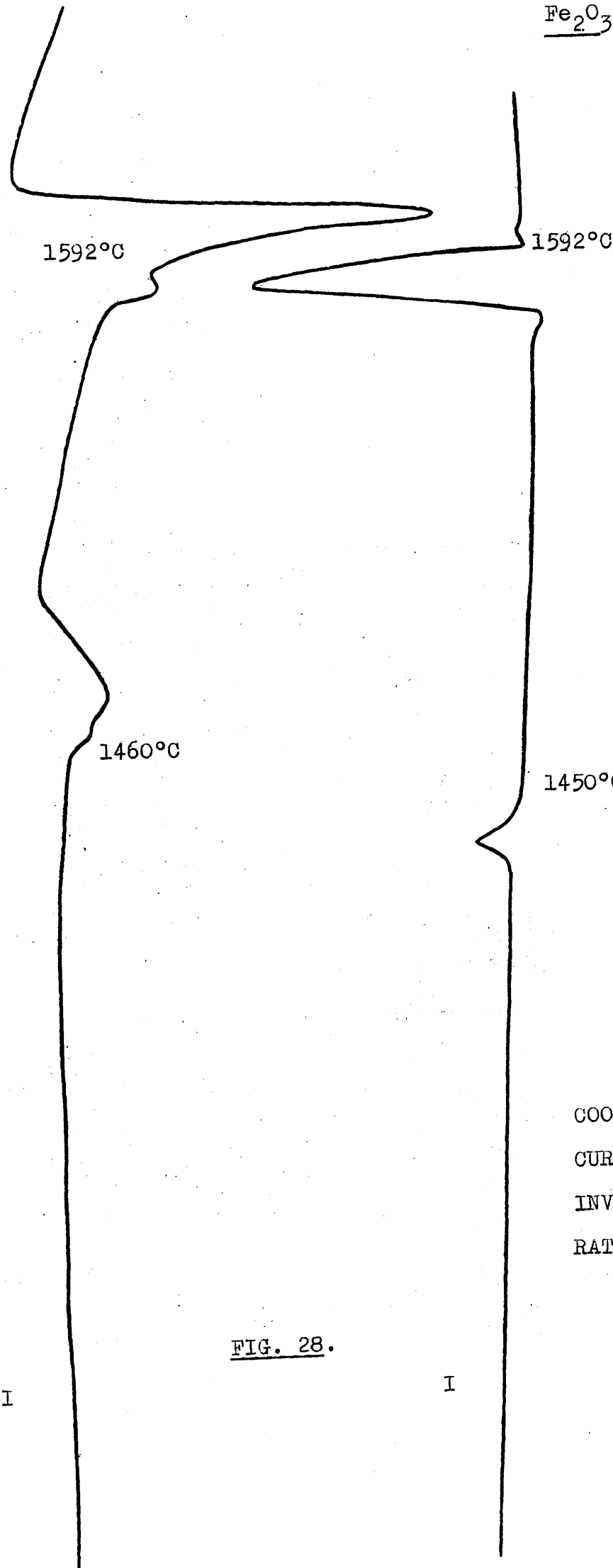

Fe_2O_3
1592°C
1592°C
1460°C
1450°C
HEATING CURVE INVERSE RATE.
COOLING CURVE - INVERSE RATE.
I
I

FIG. 28.

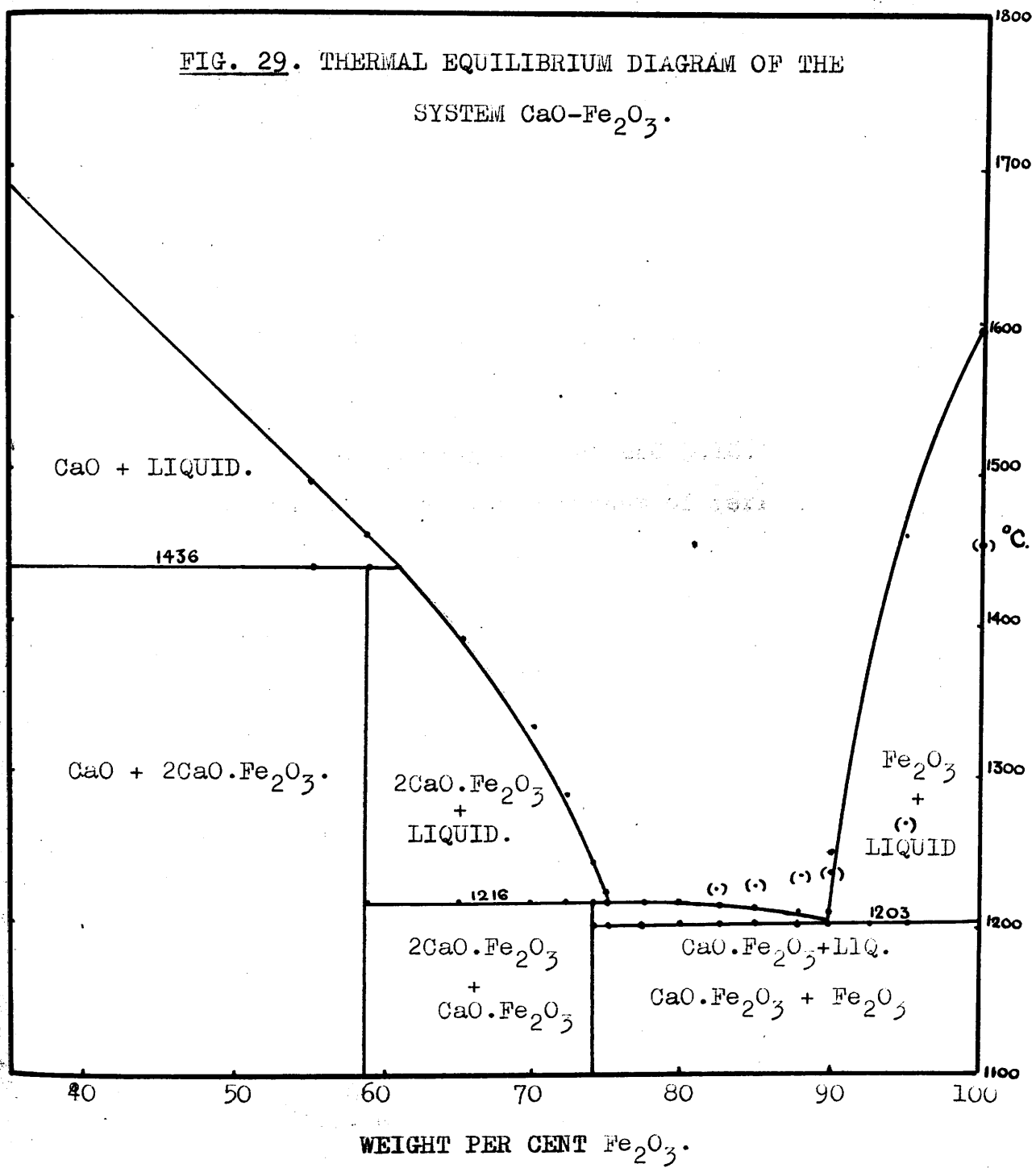
Fe_2O_3 itself was found to melt at 1595°C, but at this temperature it must have contained a considerable amount of Fe_3O_4. A pronounced arrest was obtained at 1450°C. This would probably mark the temperature at which the limiting solution of Fe_3O_4 in Fe_2O_3 would commence to dissociate on heating (see dissociation pressure curves of Fe_2O_3) under an oxygen pressure of one and a half atmospheres. At this stage in the dissociation of Fe_2O_3 a large proportion of the oxide would tend to be converted to the ferrous condition comparatively suddenly which would cause the absorption of a considerable amount of heat. Various arrests at temperatures in the neighbourhood of this are described in the literature (Benedicks and Löfquist[10]), and they have been supposed by some writers to indicate the existence of a high temperature modification of ferric oxide, but in the light of the data obtained in investigating the dissociation of Fe_2O_3 the above explanation would appear to be more probable.

The Thermal Equilibrium Diagram of the System $CaO-Fe_2O_3$.

Fig. 29 shows the thermal data obtained from the heating and cooling curves plotted in the form of a binary diagram. Evidence for the existence of two compounds only was obtained- monocalcium ferrite and dicalcium ferrite - and melts containing lime in excess of that required by the composition $2CaO.Fe_2O_3$ contained lime as a free phase. The high lime region of the diagram could not be investigated owing to the temperature limits imposed by the use of "Pythagoras" tubes. The diagram now proposed agrees very closely with that advanced by Sosman and Merwin[5], and can be taken as confirming their results both as regards the phases occurring and the temperatures of the phase changes.

The high Fe_2O_3 region (over 80% Fe_2O_3) is rather hypothetical for the reasons stated above and considerable amounts of Fe_3O_4 were always present in these melts. Calculations based on the

FIG. 29. THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM $CaO-Fe_2O_3$.



later part of the present investigations have indicated that an oxygen pressure of several thousand atmospheres would be necessary to completely inhibit dissociation in these melts. The arrests attributable to this dissociation are presented on the diagram enclosed by the signs ( ).

Optical Examination of the Melts.

This was carried out in the usual fashion and the results are tabulated below.

Fe_2O_3: Refractive index between 2.95 and 3.10. (This material would contain a variable amount of ferrous oxide.) Characterized by deep red colour in thin section.

$CaO.Fe_2O_3$: Refractive index between 2.5 and 2.6. Colour reddish brown in thin section.
The melt of monocalcium ferrite alone consisted of dark needles having a metallic lustre. They were very hard and could not be scratched with a knife.

$2CaO.Fe_2O_3$: Refractive index between 2.3 and 2.4. Light brown in colour. The dicalcium ferrite melt was tabular in appearance and was more friable than the monocalcium compound. It was also more readily soluble in hydrochloric acid.

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PART II - SECTION 11.

Investigation of the Dissociation of Ferric Oxide, Monocalcium Ferrite and Dicalcium Ferrite.

The dissociation of Fe_2O_3 at high temperatures has been investigated by several workers. Early writers specify "a white heat" as being necessary to cause loss of weight in air,[1] while, at lower temperatures, no loss took place provided reducing substances were excluded from the crucible. Several attempts have been made to detect the exact temperature at which this loss began to take place. Hofman and Mostowitsch[2] could find none after heating to 1500°C in pure dry air, and, hence, concluded that the dissociation pressure at this temperature was less than the oxygen pressure of the air. In a later publication[3] however, inspired by the results of Walden,[4] (see below), they state that Fe_2O_3 after heating to 1370°C in air was sintered but non-magnetic and contained no ferrous iron, while a sample heated to 1375°C was definitely magnetic and contained ferrous iron. Sosman and Hostetter[5], following on their work on the dissociation pressures of Fe_2O_3, carried out the same experiment under more refined conditions in a furnace fitted with a water cooled chamber into which the boat containing the oxide could be drawn to ensure rapid cooling once equilibrium had been attained. It was thus hoped to prevent the pick up of oxygen again on cooling. They concluded that a temperature in the neighbourhood of 1200°C would be sufficient to cause decomposition to begin. They pointed out the difficulties involved in arriving at an accurate figure, since they were of the opinion that, on account of the formation of solid solutions between Fe_3O_4 and Fe_2O_3, dissociation would be progressive with temperature.

Of the systemmatic attempts to investigate the dissociation pressures of Fe_2O_3 those of Walden[4] and of Sosman and Hostetter[6] are probably the most important. Walden obtained his results

by heating Fe_2O_3 in a sealed tube and measuring the equilibrium pressures developed at various temperatures. He assumed that, so long as any undissociated Fe_2O_3 was present, the resulting oxides would have a definite dissociation pressure dependent on temperature alone. Sosman and Hostetter claimed that this was not the case, and that the oxygen pressure at any temperature was also a function of the amount of ferrous iron which had been formed through dissociation. They published curves, obtained at 1100°C and 1200°C respectively, showing the variation of the dissociation pressure with the composition of the solid phase at constant temperature. These showed that a rapid fall in pressure took place with the formation of small amounts of Fe_3O_4 in the oxide. For higher amounts of Fe_3O_4 the fall became much more gradual (though in no region did the pressure ever become constant with varying composition), till a composition approaching Fe_3O_4 was reached, when a rapid decrease to a very low value took place. Sosman and Hostetter interpreted these results as indicating a complete range of solid solution between Fe_2O_3 and Fe_3O_4 at these temperatures. This has since been pointed out to be highly improbable in the light of thermal data and microscopic evidence. (see Benedicks and Löfquist[7]). One point of importance emerged from this work, namely, that the initial dissociation pressure of Fe_2O_3 was much higher than had been previously supposed.

Details of the Apparatus.

Several attempts were made to construct an apparatus suitable for this work. One of the chief difficulties encountered was to find a tube capable of maintaining a vacuum at temperatures over 1200°C, and yet of suitably small volume. Porcelain, fused silica, and small diameter "Pythagoras" tubes were all tried without success. Finally it was decided to have recourse to the larger size of "Pythagoras" tube as used in the earlier section of the work and to overcome the disadvantage of the large volume by using larger quantities of oxide.

A specially designed, horizontal, molybdenum-wound furnace large enough to take the "Pythagoras" tube was used (see Fig. 30). The open end of the tube was sealed with a three-holed rubber bung to provide for connections (1) to the Mercury pressure gauge, (2) to the "Cenco Hyvac" pump, and (3) to allow the emergence of the thermocouple leads, a vacuum-tight seal being obtained in the manner already described in Part I. A water-cooled copper coil was wound round the outside of the tube as shown, and a baffle was placed inside the tube. This served a double purpose as it kept the rubber bung practically at room temperature and, further, by maintaining the temperature in that part of the tube approximately constant, it decreased the time necessary for thermal equilibrium to be attained in the system when the temperature inside the furnace was held constant. The closed end of the "Pythagoras" tube projected only a few inches from the furnace casing. A vernier cathetometer capable of reading to .0001 cm. was employed to measure the mercury levels in the pressure gauge. Between the pump and the "Pythagoras" tube was inserted a T-piece, one leg of which was connected to a conical pressure flask and thence to an oxygen cylinder. The flask was further connected to a second pressure gauge so that, if necessary, known amounts of oxygen could be added to or withdrawn from the system, stop-cocks being provided for this purpose.

Experimental Procedure.

Dissociation of Fe_2O_3: Details of Experiments; Fe_2O_3 was prepared as already described. In commencing this work a series of preliminary experiments was carried out in which 10 grams of the oxide was spread in a thin layer in a platinum boat, but this method had to be abandoned since it was found that dissociation on heating did not take place uniformly throughout the mass. This was probably due to the existence of a slight temperature gradient which caused the dissociation to commence at one point, and to proceed progressively along the

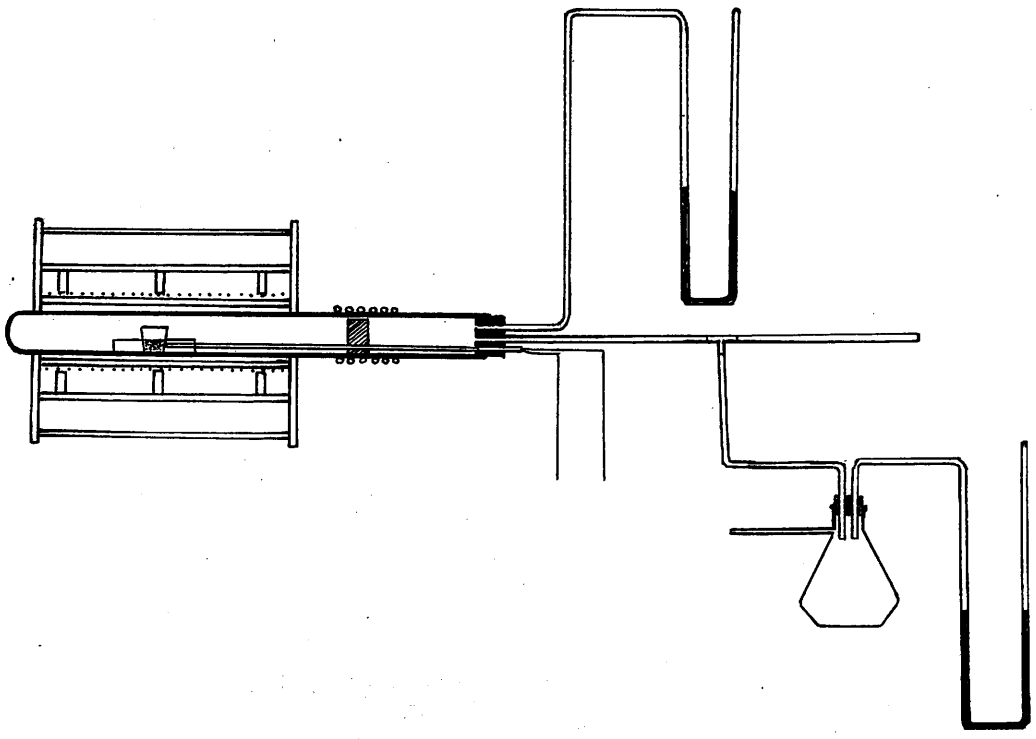


FIG. 30. DIAGRAM OF APPARATUS FOR MEASURING DISSOCIATION PRESSURES.

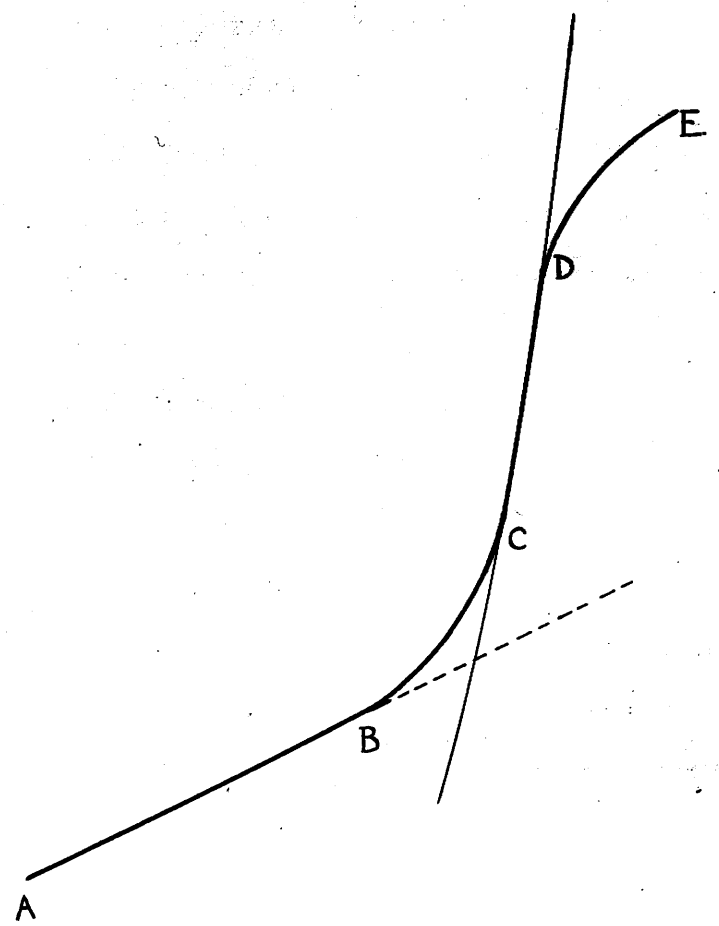


FIG. 31. EXAMPLE OF PRESSURE-TEMPERATURE CURVE WITH Fe_2O_3 IN THE TUBE.

boat as the temperature was raised. This occurrence was brought prominently to notice in one experiment when the rate of cooling had been comparatively rapid. It was found that the resultant oxide was magnetic and largely Fe_3O_4 at one end, while at the other end it was entirely Fe_2O_3. It was also found that the use of thicker layers of the material did not appreciably affect the uniformity of the mass on cooling, indicating that the charge remained sufficiently porous to admit oxygen to all parts on cooling. A platinum crucible was, therefore, substituted for the boat so that the charge might be concentrated as much as possible about a single point in the furnace. This resulted in close agreement between different runs.

The method finally adopted was to start heating the charge from room temperature with a known pressure of oxygen in the tube. In the course of the heating the temperature was held steady at suitable intervals till a state of equilibrium had been attained. The pressure was then read off by means of the gauge. As the temperature increased the pressure rose in regular fashion due solely to the thermal pressure increase of the gas in the tube, until a temperature was reached at which the dissociation pressure of the oxide was greater than that existing in the tube. A more rapid increase of pressure with temperature then took place, this being shown by a break in the pressure-temperature curve of the system. By varying the initial oxygen pressure the temperature at which this break took place could be altered. On cooling recombination with this oxygen took place and, in nearly all cases, after a run the pressure at room temperature was found to have returned to within a few millimetres of the initial value. The oxide was then found to have within narrow limits the same weight as initially and to be non-magnetic containing no detectable trace of ferrous iron.. On cooling as rapidly as possible in the furnace (which took approximately 1 hour to reach 400°C starting from 1400°C) a very slight trace of magnetism could sometimes be detected and a small amount of ferrous iron, but there was

every indication that most of the oxygen evolved could be picked up again very rapidly on cooling. In this connection it is worthy of record that, when the partly dissociated oxide was in equilibrium with the atmosphere of the tube at temperatures in the neighbourhood of 1200°C, any sudden admission of oxygen such as to raise the pressure rapidly caused an almost immediate evolution of heat, shown by a marked rise in the temperature as recorded by the thermocouple tied to the outside of the crucible. Conversely, withdrawal of oxygen under similar conditions caused an immediate drop in temperature. This appears to provide a clear indication of the rapidity with which dissociation and recombination take place.

Those runs on which the initial oxygen pressure was very low (less than 0.5 cm. of mercury) provided an exception to the generally observed behaviour in that there was evidence of small unaccountable increases in pressure on heating. These evolutions were irreversible on cooling as the gas was not picked up again, and the final pressure at room temperature was invariably higher than the initial pressure before heating. This may have been due to a gas evolution from the tube at low pressures. A slight degree of hysteresis in the equilibrium $Fe_2O_3 = Fe_3O_4 +$ oxygen at low pressures is also possible. (These samples were usually slightly magnetic.) For this reason the values obtained for the dissociation pressures of Fe_2O_3 at the lower temperatures investigated, are in all probability rather high. When freshly prepared oxide was used an irreversible gas evolution also occurred, though the material was non-magnetic on cooling. This can probably accounted for as the evolution of gases adsorbed or occluded by the oxide during its preparation.

The temperature of the room was recorded each morning, when the final pressure from the previous day's run, and the initial pressure adopted for the next run were measured. During the whole series of experiments this did not vary more than 3°C, an amount which was considered to have negligible influence on the weights of gas admitted to the tube.

By means of the furnace control adopted - two rheostats for coarse and fine adjustment respectively in parallel - together with the use of a highly sensitive galvanometer and Tinsley vernier potentiometer for temperature measurement, it was possible to maintain the temperature constant to within 1°C as long as desired. In actual practice times ranging from half an hour to one hour were allowed for the system to come to equilibrium as regards temperature distribution. This took considerably longer at temperatures under 1000°C than it did at the higher temperatures. The oxide, once it had started to dissociate, appeared to come to equilibrium with the oxygen pressure much more rapidly than the tube did thermally.

In order to determine the dissociation temperatures under different oxygen pressures, the initial pressures in the tube were varied as already described. From the preliminary experiments the following points emerged:

(1) When freshly prepared oxide was used a marked irreversible evolution of gas took place at comparatively low temperatures. This was absent on heatings, and was no doubt due to the presence of gas in the finely divided oxide when freshly prepared.

(2) At temperatures from 1100°C and upwards, depending on the initial pressure in the tube, the pressure began to rise more rapidly with temperature, and continued to do so at an increasing rate as the temperature was still further raised. This evolution was strictly reversible on cooling. It was also observed that,, where a small amount of oxide was used, or where the initial pressure was very low, at still higher temperatures than the above there was again a lowering of the rate at which pressure increased with temperature. The type of curve obtained is shown in Fig. 31.

(3) When the results were plotted on a pressure-temperature diagram it was found that the steepest parts of all the curves lay along a common envelope curve.

A number of these pressure-temperature curves have been

plotted in Fig. 32a and 32b. Over 40 different curves were determined with varying initial pressures and varying amounts of oxide. It will be observed that all converge on the same limiting curve. The upper temperature to which these curves could be taken was limited in many cases by the tendency of of the tubes to collapse at high temperatures when the pressure inside was much below atmospheric. With the higher oxygen pressures a higher temperature could be attained though this was still limited. On the other hand the maximum pressure it was considered safe to employ at the higher temperatures was roughly one and a half atmospheres.

The interpretation of these results is given as follows. Referring to Fig. 31, the first uniform portion, AB, of all curves results from the increase in temperature of the gas already in the tube. The pressure of oxygen in the tube in this region is presumably greater than the dissociation pressure of the oxide so that no dissociation occurs. As the temperature is increased, a point B is reached at which the dissociation pressure becomes greater than the oxygen pressure in the tube and an evolution of oxygen accordingly takes place, accompanied by a corresponding rise in pressure. There is, therefore, an increase in the rate at which pressure increases with temp - erature. This is at first gradual but later increases in rapidity as shown by the curves till it attains an approximately constant value. Thus the pressure-temperature curves show two distinct parts in this region, (1) a curved portion, BC, where the <u>rate of pressure increase</u> is increasing, and (2) a steep portion, CD, where the <u>pressure</u> is increasing rapidly though the rate of increase is fairly constant. On some of the curves a third portion, DE, is shown where the <u>rate of pressure increase</u> again falls off. The steep parts of all the curves can be imposed on the same envelope curve, and apparently indicate the existence of a definite phase, whose dissociation pressure is dependent only on temperature, and is independent of the amount present. This phase cannot be pure Fe_2O_3 as a

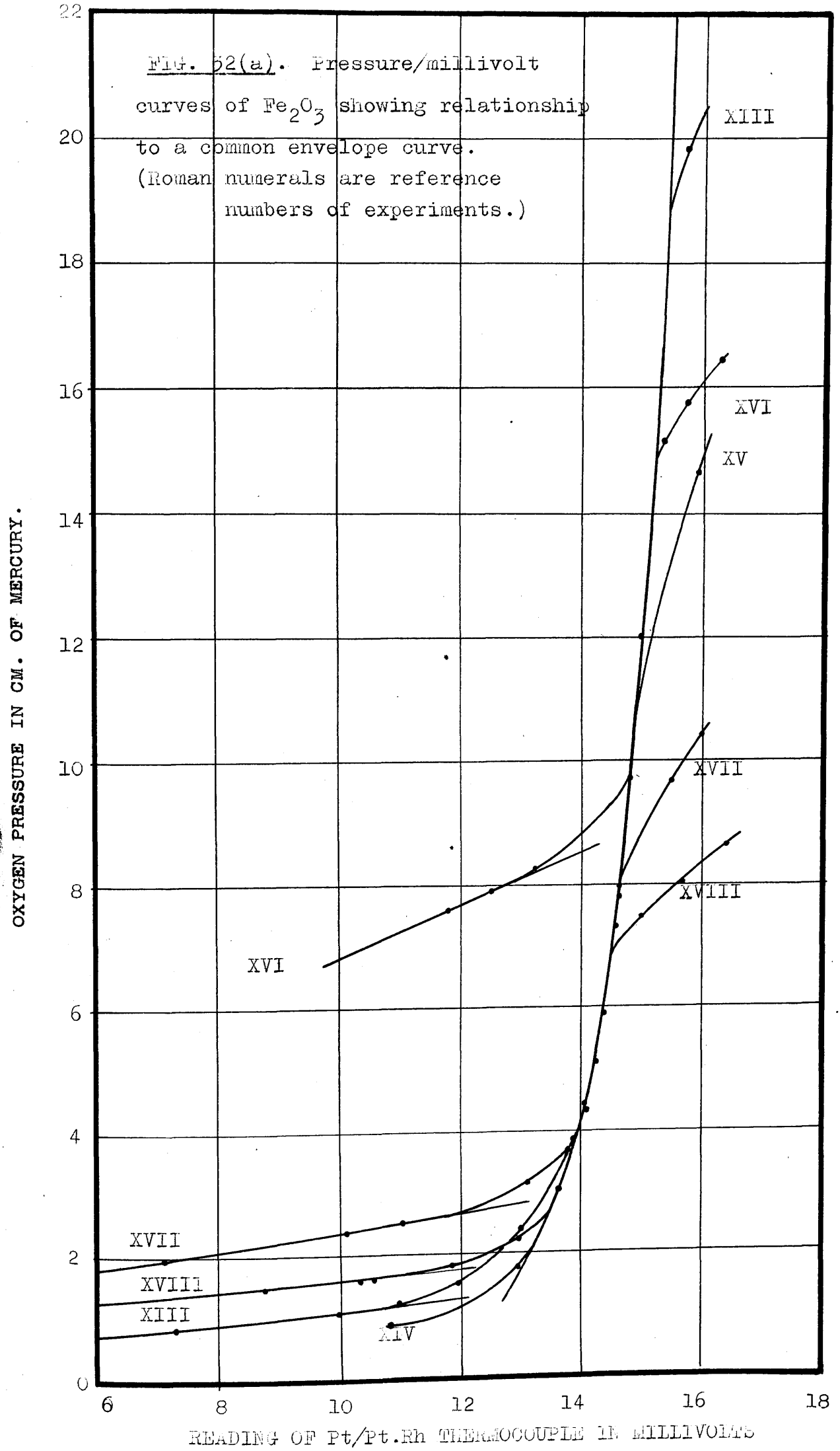
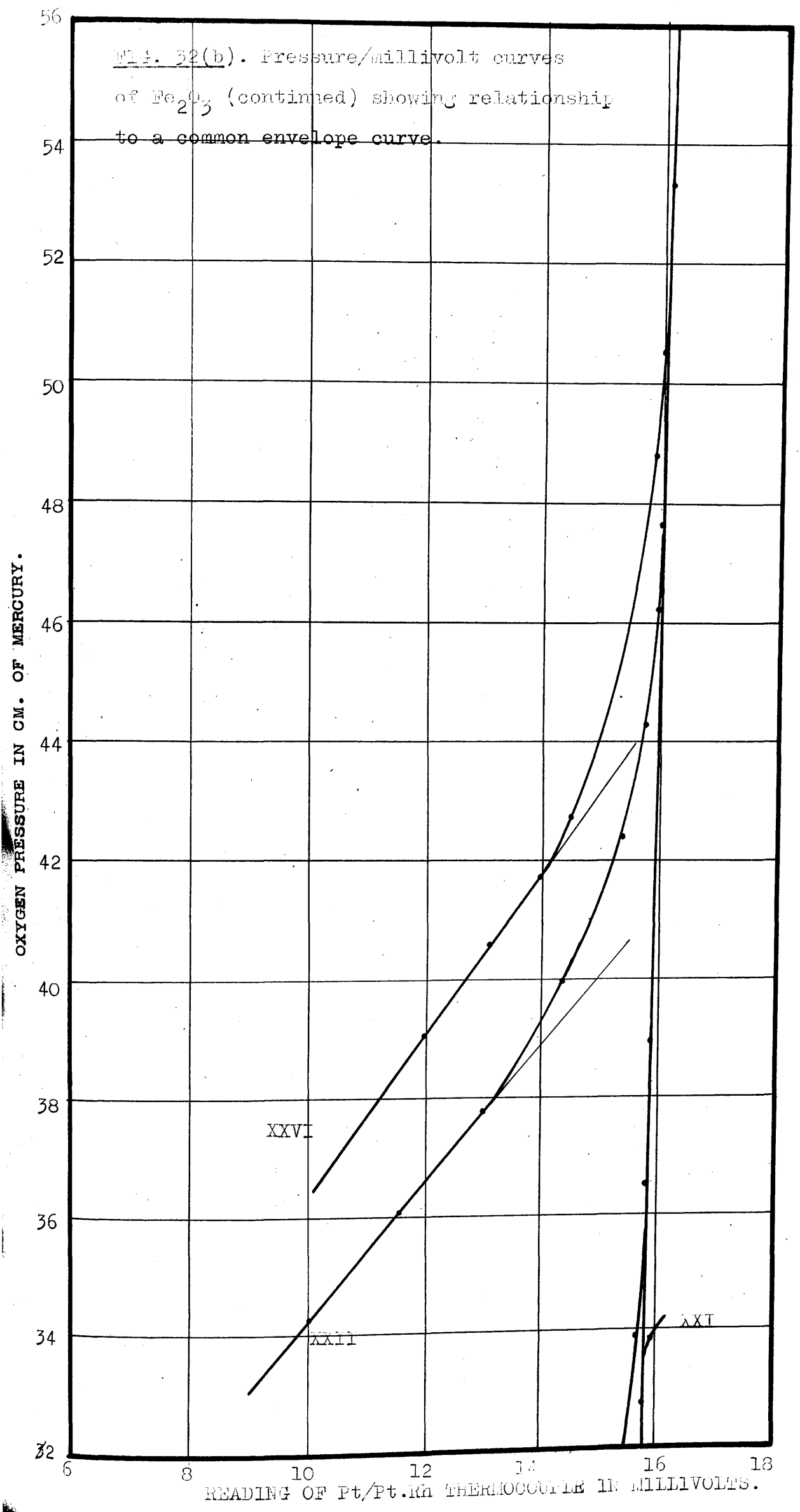


Fig. 52(a). Pressure/millivolt curves of Fe_2O_3 showing relationship to a common envelope curve. (Roman numerals are reference numbers of experiments.)
XIII
XVI
XV
XVII
XVIII
XVI
XVII
XVIII
XIII
XIV
OXYGEN PRESSURE IN CM. OF MERCURY.
0
2
4
6
8
10
12
14
16
18
20
22
6
8
10
12
14
16
18
READING OF Pt/Pt.Rh THERMOCOUPLE IN MILLIVOLTS

Fig. 32(b). Pressure/millivolt curves of Fe_2O_3 (continued) showing relationship to a common envelope curve.



considerable amount of oxygen has already been evolved as shown by the preceding portion of the curve BC. Further in this latter portion BC the pressure-temperature values are peculiar to the individual curve on which they appear, and the value of the pressure at any point appears to depend on the amount of dissociation which has already taken place in the oxide. In other words it would appear that the pressure in this region is a function of the composition of the solid as well as of temperature. Hence it follows, from consideration of the Phase Rule, that the substance formed on the liberation of the first portion of the oxygen from the Fe_2O_3 must be soluble in the remaining Fe_2O_3. Finally, when the limit of solubility has been reached, a phase of definite composition exists and further dissociation is accompanied by the formation of a new phase. The first phase will be a solution of Fe_3O_4 in Fe_2O_3; the second of Fe_2O_3 in Fe_3O_4. The complete dissociation of the Fe_2O_3-rich phase would result in a marked deviation from the common envelope curve, and this is shown in those curves in which the conditions were suitable for this degree of dissociation to be attained. The curve showing the variation in the dissociation pressure of the saturated solution of Fe_3O_4 in Fe_2O_3 is well marked by the envelope curve. It is less easy to pick out the points on the various curves at which initial dissociation begins. This has been done by taking the points where the break in direction appears to originate. The points so obtained have been plotted in the form of a curve of initial dissociation pressure against temperature. It is quite possible that a small amount of dissociation occurs before oxygen evolution becomes measurable under the conditions of experiment, in which case the true initial dissociation pressures would be somewhat higher than indicated by the curve. Both curves are reproduced in Fig. 33. On this diagram are also plotted the values which were experimentally determined by Walden (l.c.) and published as the dissociation pressures of ferric oxide. It will be observed that these

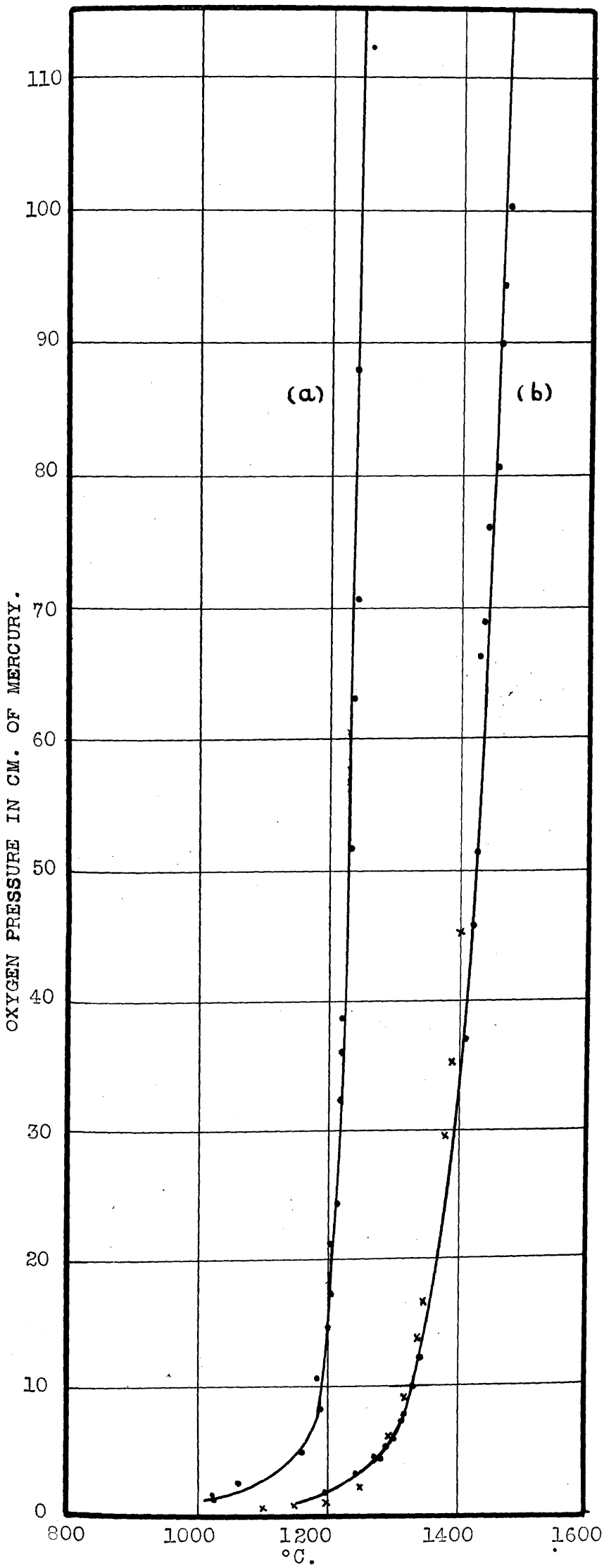


FIG. 33. DISSOCIATION-PRESSURE/TEMPERATURE CURVES OF Fe_2O_3.

(a) Initial Dissociation Pressure.

(b) Dissociation Pressure of Saturated Solution of Fe_3O_4 in Fe_2O_3.

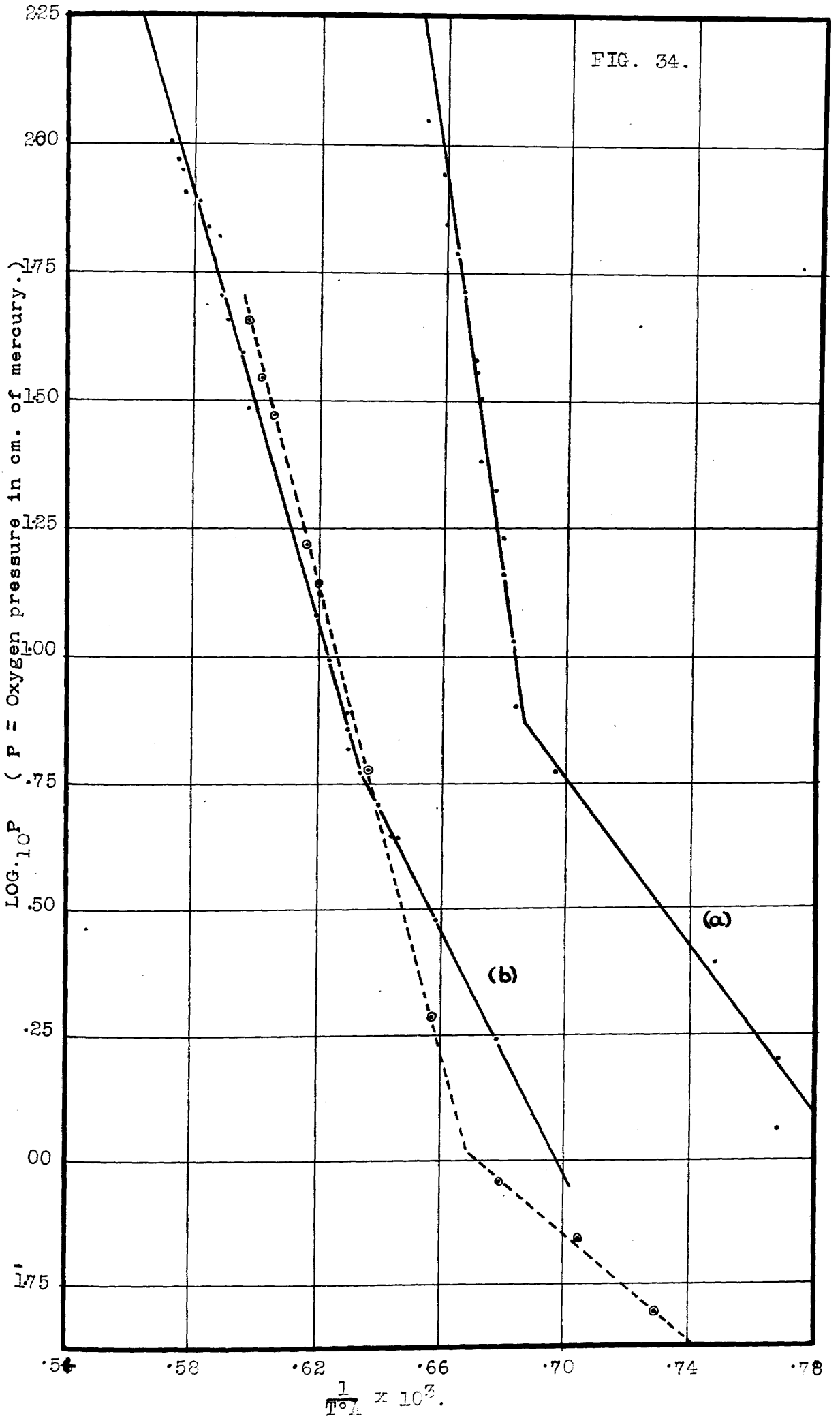
(× Walden's Data.)

values are in very good agreement with the curve now given for the dissociation of the limiting solid solution of Fe_3O_4 in Fe_2O_3. Consideration of the method employed by Walden indicates that it is highly probable that the pressures which he measured were those of the limiting solid solution, and therefore his work provides confirmation of the present results. The pressure values on the curve of initial dissociation at 1100°C and 1200°C also agree reasonably well with the values indicated by the isotherms of Sosman and Hostetter (l.c.) as far as can be judged.

The experimental values have also been plotted in Fig. 54 in the form of the logarithm of the pressure against the reciprocal of the absolute temperature, curve (a) being that of the initial dissociation and curve (b) that of the limiting solution. Both curves appear to be linear except for the four lowest values in each case (representing pressures of less than five centimetres of mercury), which are apparently too high. The fact that the deviations so produced would appear to be themselves linear in nature is suggestive of some physical meaning, but, as previously mentioned, these very low values are not above suspicion on account of abnormal gas evolution in the tube. A special apparatus would be required to investigate this region owing to the difficulties involved in working with extremely low pressures at high temperatures. Walden's values are also plotted on this diagram and, rather peculiarly, they also show a deviation, though this occurs at a somewhat lower pressure than in the curves derived from the present experiments.

A series of pressure-composition isotherms was constructed from the pressure-temperature curves. The method adopted was to calculate, from a consideration of all the curves, an "expansion factor" representing the ratio in which the pressure of the original gas in the tube increased between room temperature and each of the isothermal temperatures selected. This was rendered necessary by the temperature variation existing throughout the system. The agreement between the various curves in this respect was very satisfactory. An exception

FIG. 34.


225
200
175
150
125
100
·75
·50
·25
00
1·75
LOG.10P (P = Oxygen pressure in cm. of mercury.)
·54
·58
·62
·66
·70
·74
·78
1/T°A x 10³.
(a)
(b)

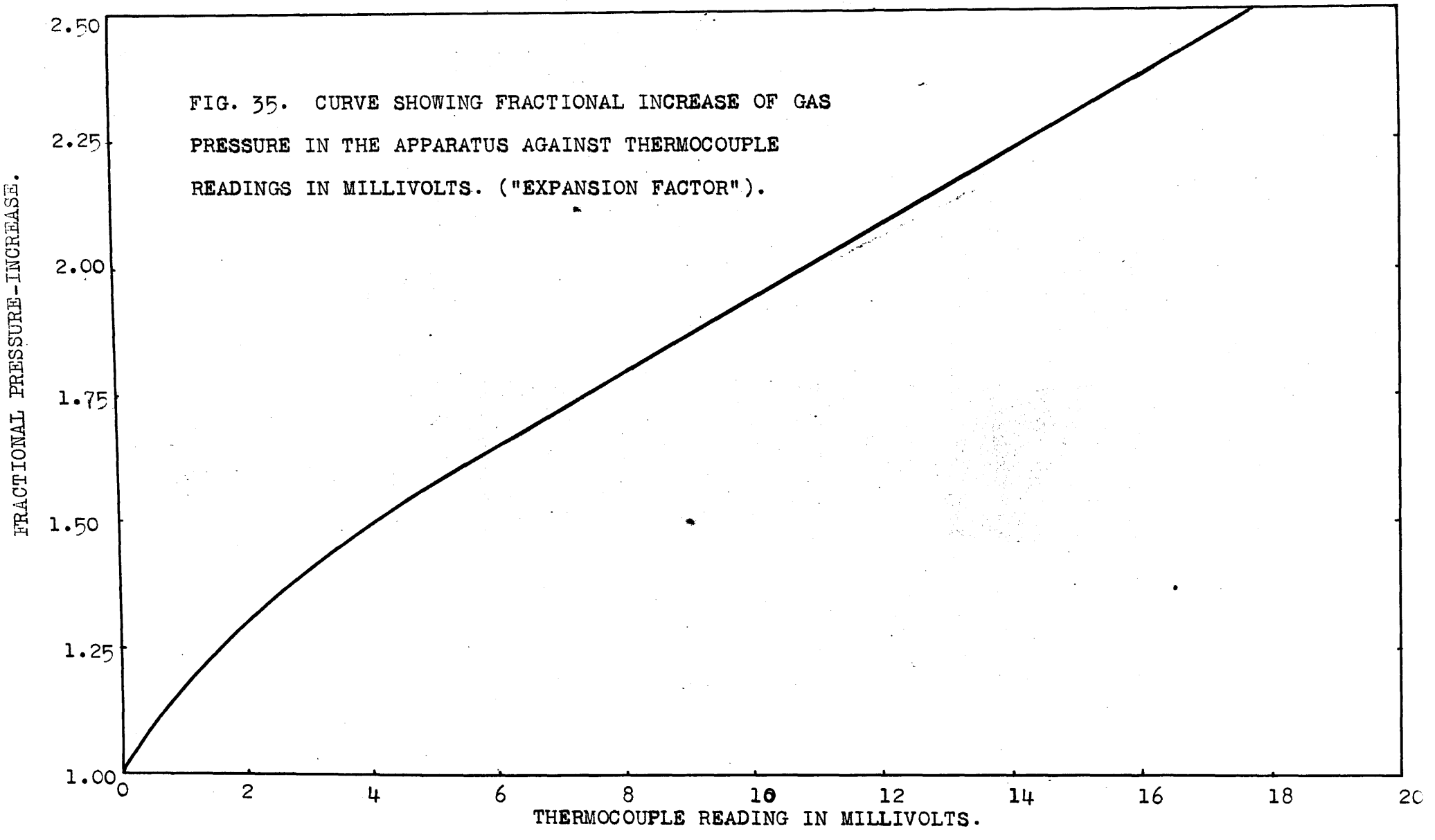


FIG. 35. CURVE SHOWING FRACTIONAL INCREASE OF GAS PRESSURE IN THE APPARATUS AGAINST THERMOCOUPLE READINGS IN MILLIVOLTS. ("EXPANSION FACTOR").

must be made in the case of those curves obtained with very low initial pressures in the tube, when as already described, abnormal gas evolutions took place. A check on the value of the "expansion factor" was got by running blank experiments with only oxygen in the tube. Fig. 35 shows the variation of this factor with increasing millivolt readings of the thermocouple. A value for the volume of the apparatus was got by measuring the pressure in the tube before and after the admission of a known volume of oxygen to the system. It was then possible to calculate the weight of oxygen liberated from the oxide for any temperature and pressure on the curves. For this purpose the initial "thermal pressure-increase" part of each curve was produced to enable the pressure increase due to the dissociation to be obtained. This procedure was made possible owing to the fact that over the range of temperature concerned, 1100°C to 1500°C, the pressure increase with temperature approached very closely to linearity, as shown in Fig. 35. The proportion of ferrous iron present in the solid phase could then be calculated for various temperatures and pressures. Further details concerning the calculation of these isotherms are given in the appendix. Fig. 36 shows the pressure-composition isotherms for the temperatures 1200°C, 1272°C, 1345°C, and 1415°C. Whilst the absolute accuracy of the compositions given in this diagram will depend upon the accuracy with which the "expansion factor" has been determined, the relative agreement of the points on each isotherm is independent of this factor. The close agreement of these points can, therefore, be taken as proof of the validity of this method. In Fig. 37 the data concerning solubility limits obtained from these isotherms has been plotted on the phase diagram of the system Fe_2O_3-Fe_3O_4 given qualitatively by Benedicks and Löfquist (l.c.). Additional points have been calculated from the individual pressure-temperature curves from a consideration of the amounts of oxygen evolved in the tube at the points at which the various curves approach or leave the envelope curve. These values are

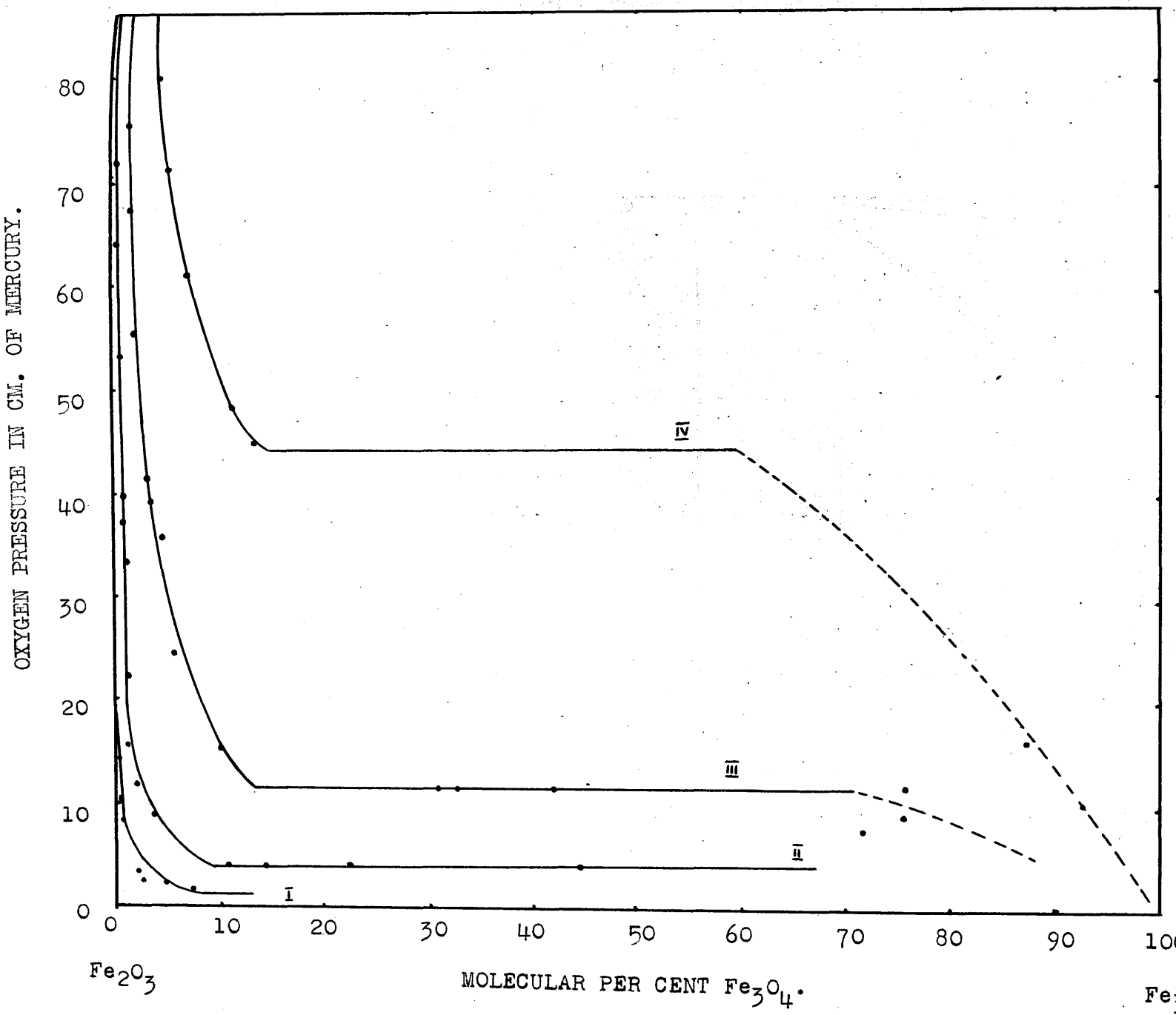


FIG. 36. PRESSURE/ COMPOSITION ISOTHERMS OF THE SYSTEM Fe_2O_3-Fe_3O_4.

I - Isotherm at 1200°C.

II- Isotherm at 1272°C.

III-Isotherm at 1345°C.

IV- Isotherm at 1415°C.

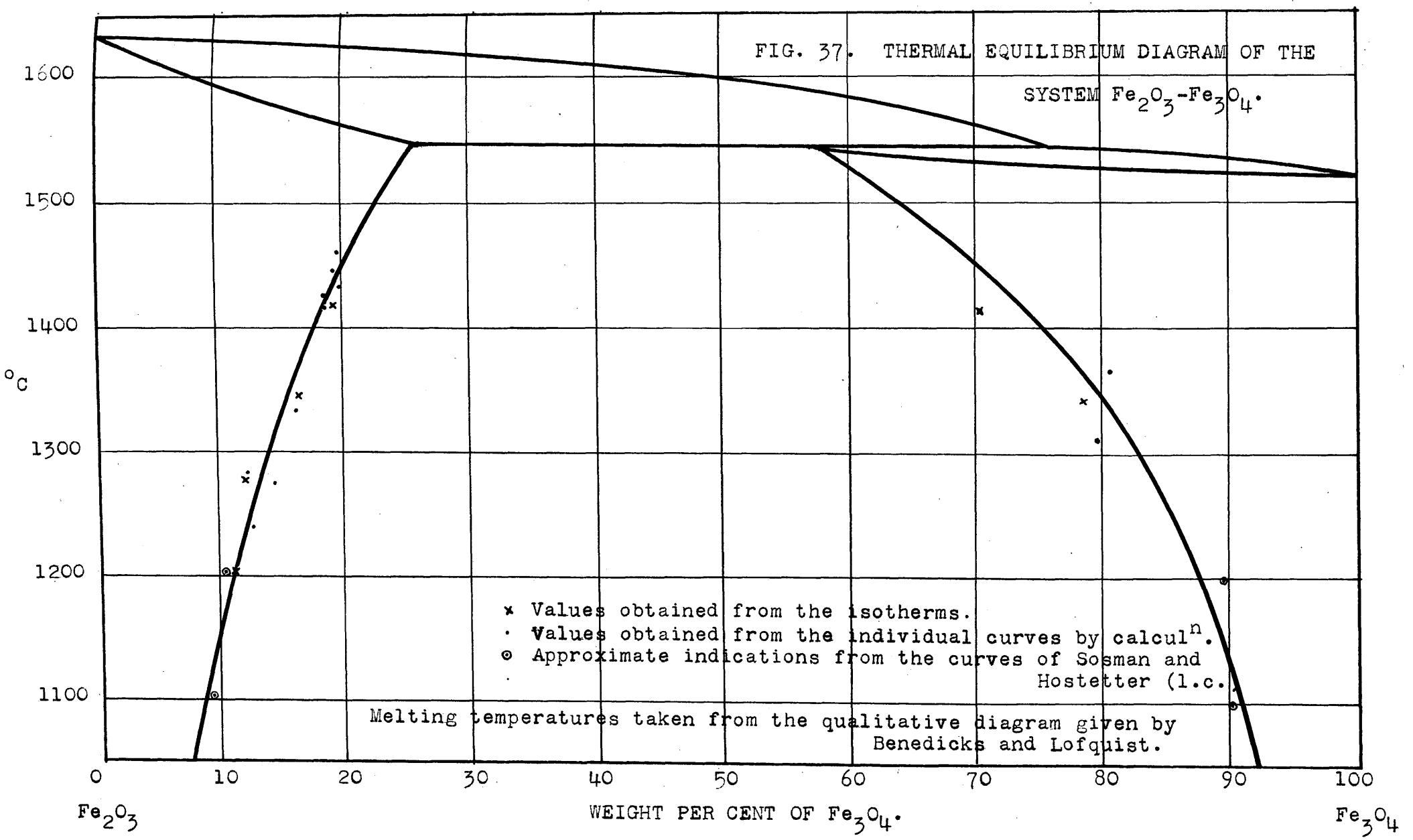


FIG. 37. THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM Fe_2O_3-Fe_3O_4.
1600
1500
1400
°C
1300
1200
1100
0
10
20
30
40
50
60
70
80
90
100
Fe_2O_3
WEIGHT PER CENT OF Fe_3O_4.
Fe_3O_4
× Values obtained from the isotherms.
· Values obtained from the individual curves by calcul^{n}.
⊙ Approximate indications from the curves of Sosman and Hostetter (l.c.).
Melting temperatures taken from the qualitative diagram given by Benedicks and Lofquist.

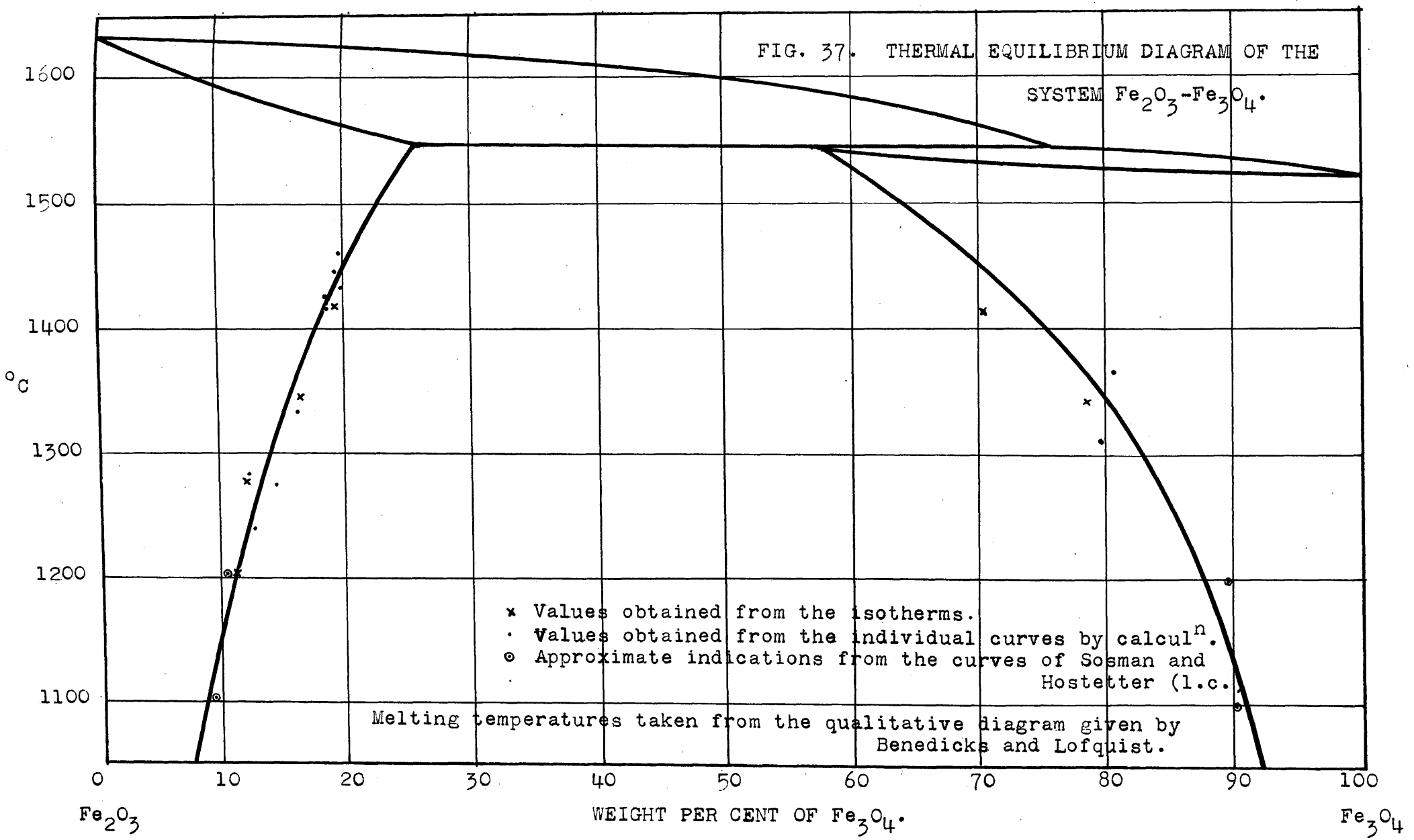


FIG. 37. THERMAL EQUILIBRIUM DIAGRAM OF THE SYSTEM Fe_2O_3-Fe_3O_4.

also plotted on Fig. 36. Approximate values indicated by the isotherms of Sosman and Hostetter, on the assumption that the central portions of their curves should have been horizontal are also given.

Addendum: It is rather difficult to correlate these results with the published work of Sosman and Hostetter (l.c.). The two isotherms given by these workers indicate very high initial dissociation pressures for pure Fe_2O_3 and in this respect may be said to agree with the present results. The central portions of their isotherms are by no means horizontal though they are considerably flatter than the extremities. Further the change in direction is gradual, with no signs of discontinuity, so that it is difficult to select positions at which it may be said to originate. The pressure values on this flatter part of the 1200°C isotherm range from roughly 4 m.m. of mercury pressure down to 1 m.m. (the value towards the centre is approximately 2 m.m.). On substituting these values on a continuation of the logarithmic diagram given in Fig. 34 it is found that the highest of them (4 m.m. pressure) is slightly lower than the value indicated by the upper part of curve (b) when produced to the position corresponding to a temperature of 1200°C. The values on the central portion of the 1100°C isotherm are related to curve (b) in roughly the same way. The work of Sosman and Hostetter was carried out with great attention to detail in an apparatus specially constructed to operate accurately at very low pressures. Since the values taken above lie so close to the extension of the upper part of curve (b) it seems to confirm that the deviations found in the lower parts of curves (a) and (b) and in Walden's curve are due to errors inherent in the apparatus which manifest themselves at low pressures.

It is rather difficult to explain the exact form of the Sosman and Hostetter curves, however, unless it be postulated

that the system Fe_2O_3-Fe_3O_4 is subject to a form of hysteresis at low temperatures (1100°C and 1200°C), or that traces of some impurity, causing progressive depression of the pressure as the concentration of the Fe_2O_3 decreased, were present in the iron oxide. The presence of even slight temperature gradients throughout the mass of the sample taken could probably have produced the same effect as has already been noted.

THE EFFECT OF CaO ON THE DISSOCIATION OF Fe_2O_3: THE DISSOCIATION PRESSURES OF THE CALCIUM FERRITES.

In the investigation of the dissociation of the calcium ferrites the same technique was employed as has already been described in the case of the work on Fe_2O_3. At first the compound was prepared as a separate operation, but later the requisite amounts of CaO and Fe_2O_3 were mixed together, put into a platinum crucible and heated to a suitable temperature under a pressure of 1½ atmospheres of oxygen. On cooling the material was ready for investigation. For reasons given later this cooling had to be carried out very slowly, at least until freezing was complete.

Monocalcium Ferrite: On heating monocalcium ferrite in vacuo no measurable pressure was developed till the incongruent melting point (see the thermal equilibrium diagram of the system $CaO-Fe_2O_3$, Fig. 29) was reached. At this temperature (1216°C) a sudden increase in pressure took place, shown by a definite step in the pressure-temperature curve. The pressure obtained after this gas evolution was not, of course, the equilibrium pressure of the pure fused compound as FeO (or Fe_3O_4) would be formed by the process of dissociation. The actual pressure developed was found to depend on the weight of the calcium ferrite taken and also on the volume of the apparatus. It was thus evident that considerations similar to those governing the dissociation of Fe_2O_3 applied and that the ferrous oxide formed went into solution, the dissociation of this solution being a function of composition as well as of temperature Runs were, therefore, made with varying initial pressures of oxygen in the tube as was done in the investigation of Fe_2O_3. It was found that,as the initial pressure was increased, a value was ultimately reached at which the break in the pressure/temperature curve was displaced to a higher temperature. This appears to occur as nearly as could be determined, at a pressure of approximately 24 cm. of mercury. This has, therefore,

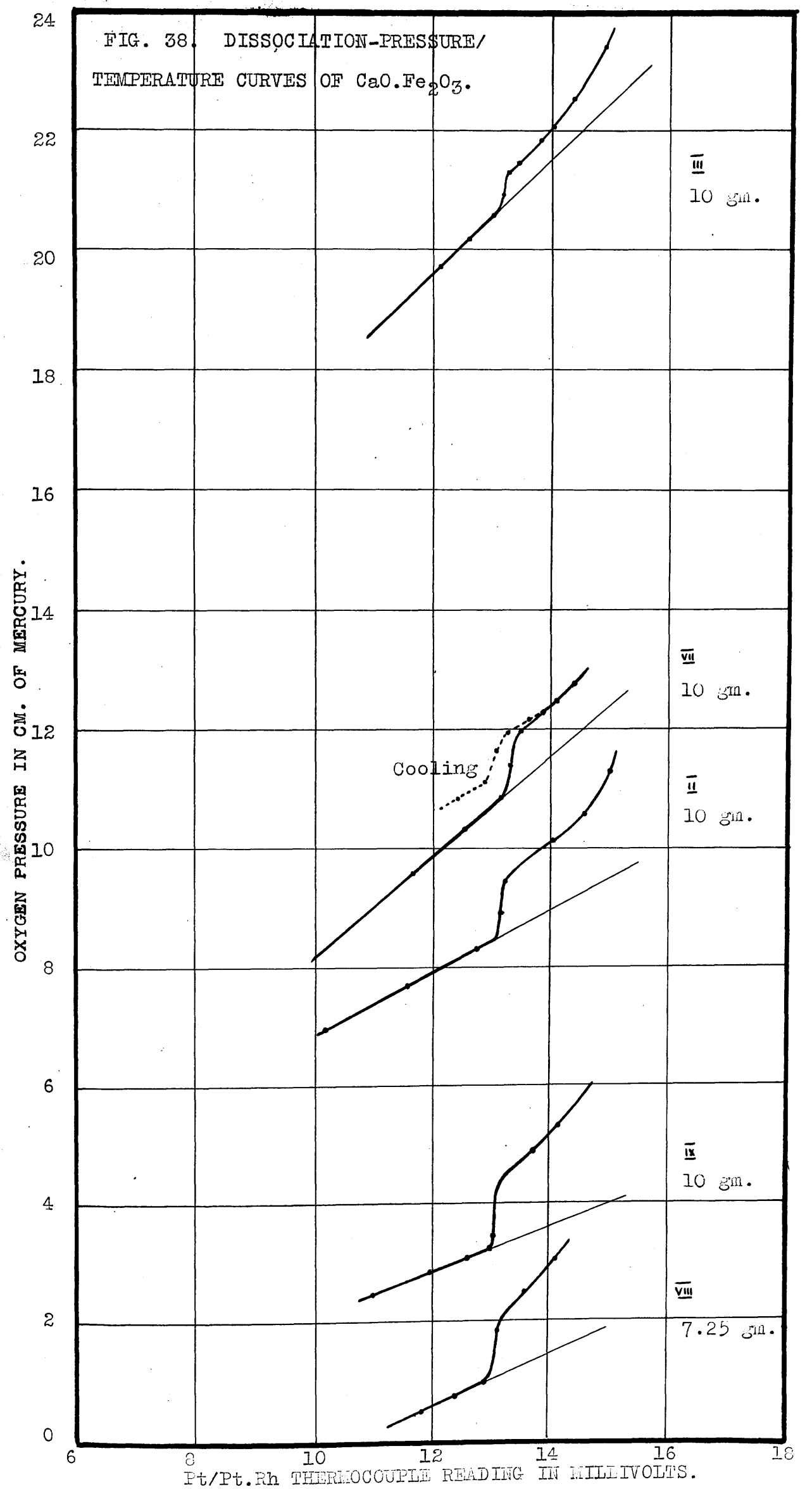


FIG. 38. DISSOCIATION-PRESSURE/ TEMPERATURE CURVES OF CaO.Fe2O3.
III
10 gm.
VII
10 gm.
Cooling
II
10 gm.
IX
10 gm.
VIII
7.25 gm.
OXYGEN PRESSURE IN CM. OF MERCURY.
0
2
4
6
8
10
12
14
16
18
20
22
24
6
8
10
12
14
16
18
Pt/Pt.Rh THERMOCOUPLE READING IN MILLIVOLTS.

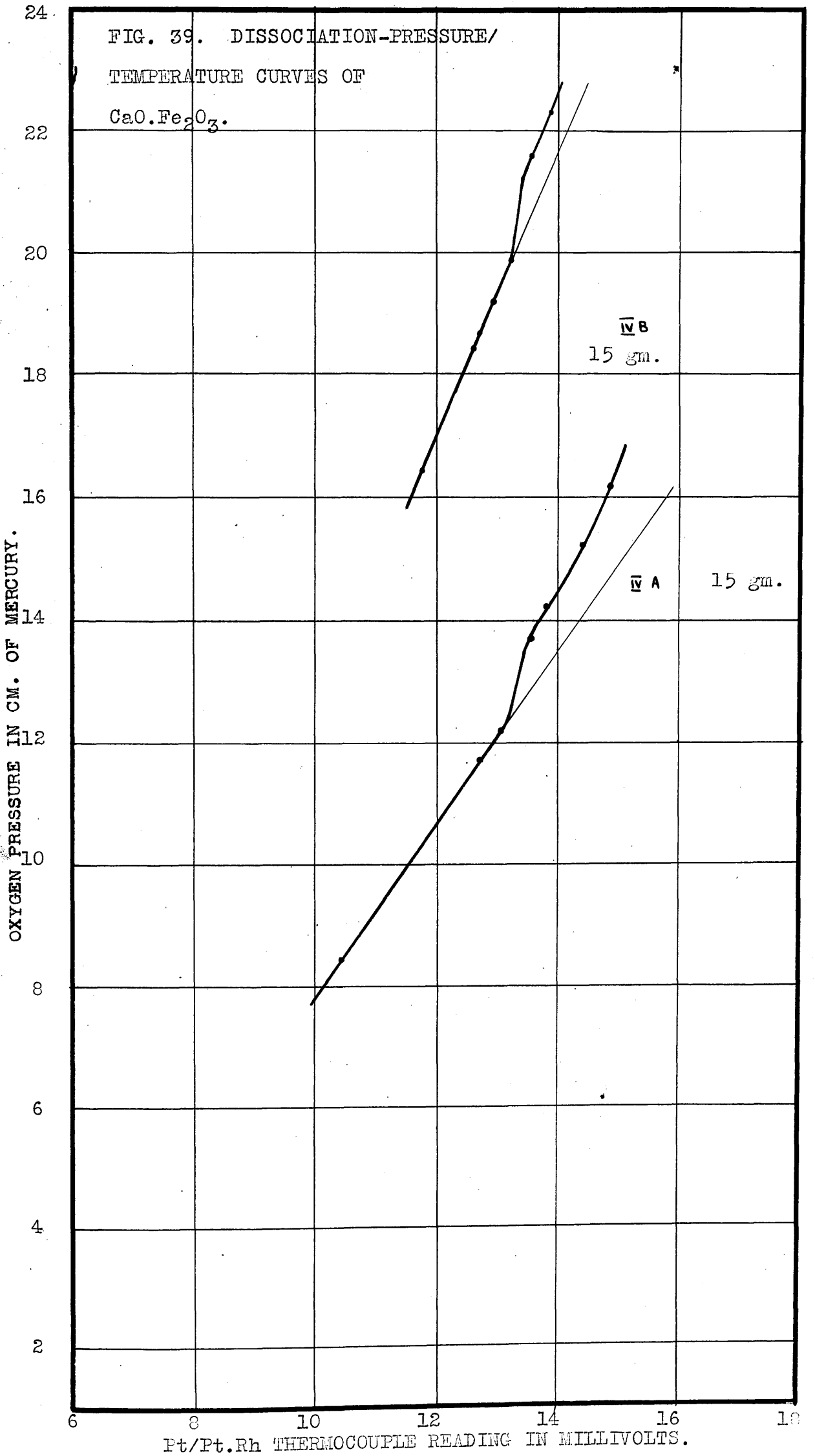


FIG. 39. DISSOCIATION-PRESSURE/
TEMPERATURE CURVES OF
CaO.Fe2O3.
IV B
15 gm.
IV A
15 gm.
OXYGEN PRESSURE IN CM. OF MERCURY.
24
22
20
18
16
14
12
10
8
6
4
2
6
8
10
12
14
16
Pt/Pt.Rh THERMOCOUPLE READING IN MILLIVOLTS.

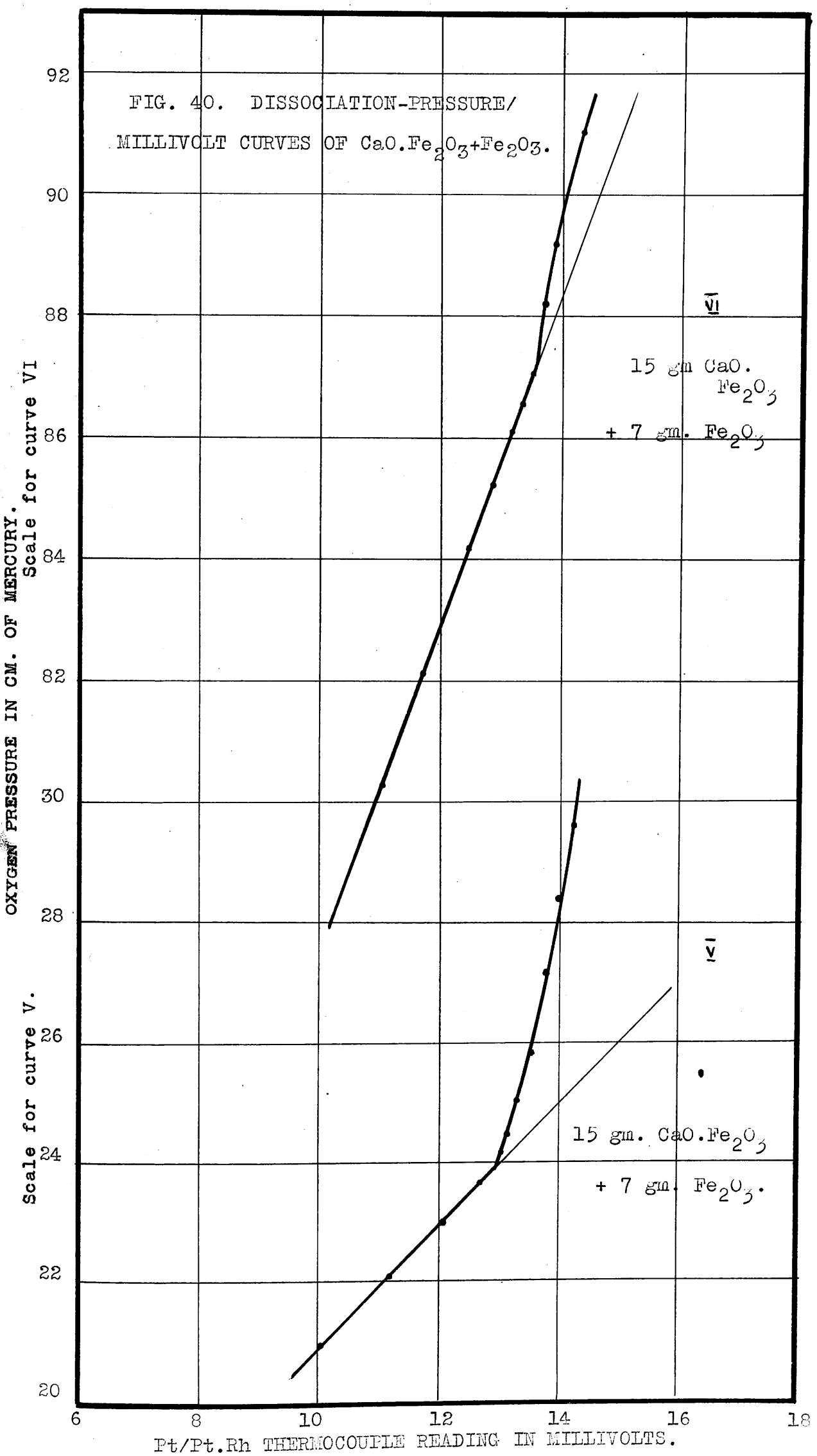


FIG. 40. DISSOCIATION-PRESSURE/
MILLIVOLT CURVES OF CaO.Fe2O3+Fe2O3.
VI
15 gm CaO.
Fe2O3
+ 7 gm. Fe2O3
V
15 gm. CaO.Fe2O3
+ 7 gm. Fe2O3.
OXYGEN PRESSURE IN CM. OF MERCURY.
Scale for curve VI
Scale for curve V.
92
90
88
86
84
82
30
28
26
24
22
20
6
8
10
12
14
16
18
Pt/Pt.Rh THERMOCOUPLE READING IN MILLIVOLTS.

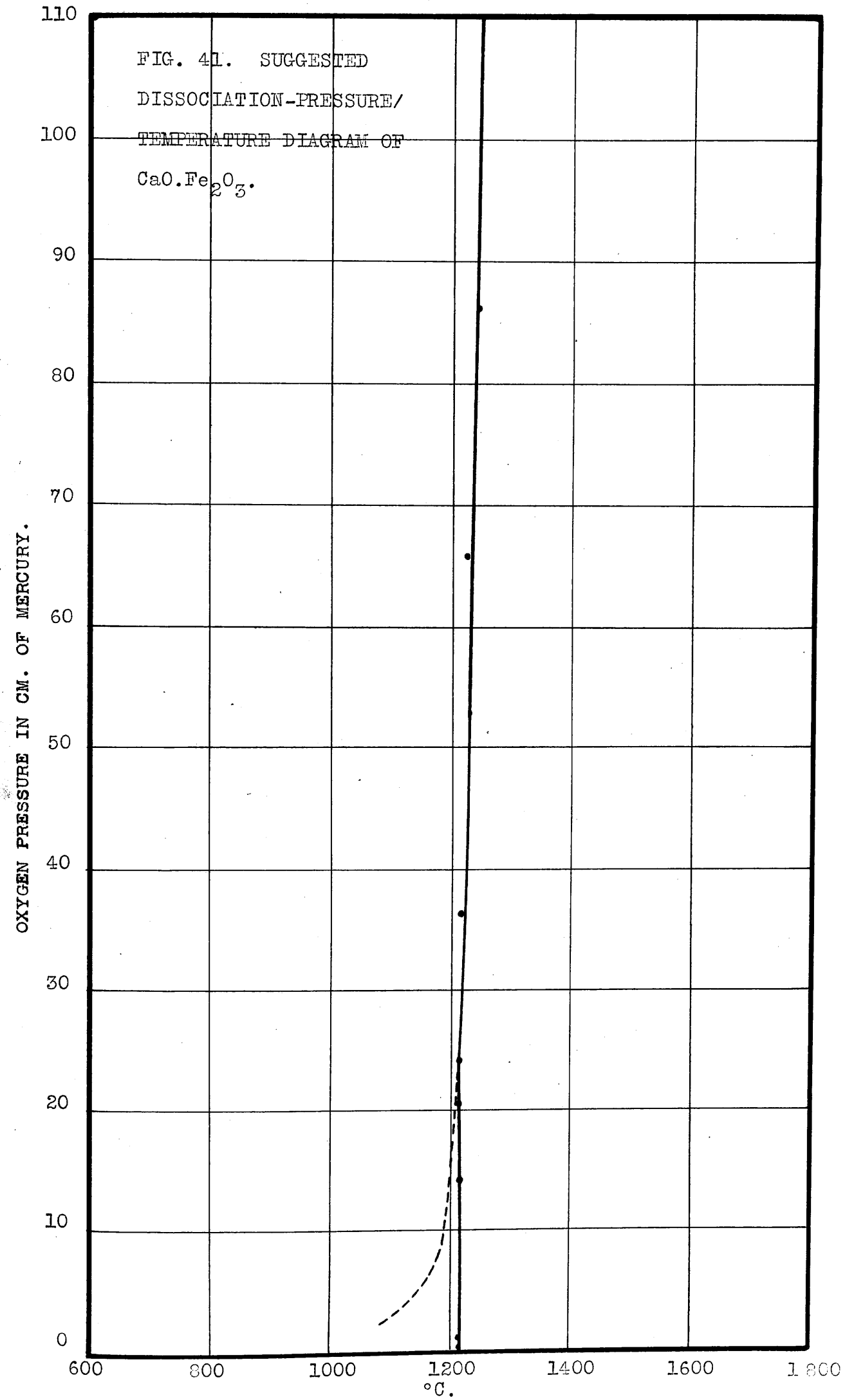
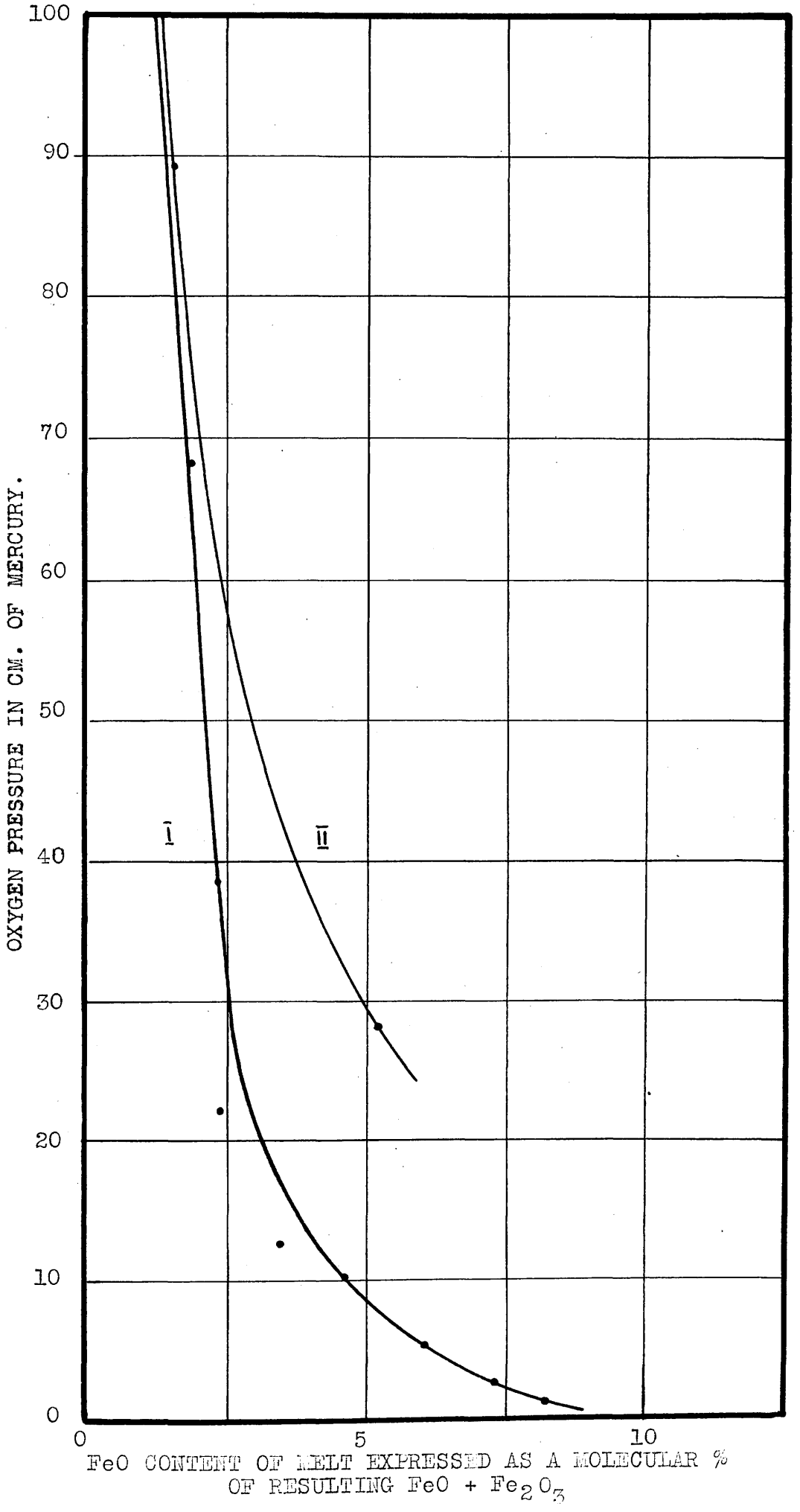


FIG. 41. SUGGESTED DISSOCIATION-PRESSURE/ TEMPERATURE DIAGRAM OF CaO.Fe2O3.
OXYGEN PRESSURE IN CM. OF MERCURY.
110
100
90
80
70
60
50
40
30
20
10
0
600
800
1000
1200
1400
1600
1800
°C.

FIG. 42. PRESSURE/COMPOSITION CURVES OF $CaO-Fe_2O_3$ MELTS AT 1272°C. Curve I. 1 Mol. CaO : 1 Mol.Fe_2O_3+FeO.

Curve II.1 Mol.CaO : 1·64 Mol.Fe_2O_3+FeO.



been taken as the dissociation pressure of $CaO.Fe_2O_3$ at the temperature at which it undergoes the peritectic transformation indicated by the phase diagram. For higher oxygen pressures the break in the curve appears to be displaced to progressively higher temperatures, though the rate of temperature rise with pressure increase is so small that it is difficult to determine exactly. A number of the individual pressure/temperature curves are shown in Figs. 38 and 39 the weight of material used being indicated in each case. The dissociation pressure/temperature curve obtained from the breaks in the various individual curves is shown in Fig. 41. The upper portion of this curve probably coincides with the curve of initial dissociation pressure of Fe_2O_3, part of this shown by the broken line. This would appear to verify the peritectic dissociation indicated by the phase diagram, the pressure recorded being due to the dissociation of the free Fe_2O_3 liberated at the peritectic. Below the peritectic temperature the dissociation pressure is probably immeasurably small due to the stability of the compound. It was further observed that, for a given temperature above the peritectic, the amount of oxygen liberated, as shown by the size of the step on the curve, decreased as the total pressure increased, indicating that the amount of dissociation depends on the oxygen pressure over the liquid melt. It was demonstrated by very slow rates of cooling that the change was reversible (see curve VII, Fig. 38), although with some difficulty, only a portion of the liberated oxygen being generally picked up under the pressure at which it was given off. From a consideration of Fig. 41 it is clear that under low oxygen pressures the pick up of oxygen can occur only when the actual temperature of freezing is reached. Hence oxidation and freezing must be proceeding simultaneously thus increasing the difficulty of oxygen pick up.

In this connection a complication arose which would tend to make the apparent dissociation too great. In order to obtain as nearly 100% $CaO.Fe_2O_3$ as possible for these experiments

the molten material was always allowed to freeze as slowly as possible under a pressure of 1½ atmospheres of oxygen. It was discovered that in freezing oxygen was very often entrapped within the melt. This oxygen was then liberated during the next heating under a lower pressure and resulted in a slow rise of pressure below the melting point, or (presumably), when it could not be detected, as an increased oxygen evolution on melting. This fact was only realised when one of the platinum crucibles was "ballooned out" due to the internal pressure.

From the individual pressure/temperature curves shown in Figs. 38 and 39 it was possible, as in the case of Fe_2O_3 to measure the amounts of oxygen evolved by the various melts at a given temperature and hence by calculation to find the amount of FeO or Fe_3O_4 formed in each case before equilibrium was attained. Further when melts were run with a greater proportion of Fe_2O_3 than required for the composition $CaO.Fe_2O_3$ dissociation began at a lower temperature, due presumably to the free Fe_2O_3 and in addition an increased amount of dissociation was obtained for a given equilibrium pressure at the temperature selected (1272°C). Moreover this increase could not be accounted for quantitatively by the dissociation of the added Fe_2O_3 as such. It is apparent, therefore, that the amount of lime is also a factorin the equilibrium in addition to temperature and oxygen pressure. For the purposes of graphical representation, the FeO formed in the melt was expressed as a molecular percentage of the total FeO + Fe_2O_3 for a given molecular ratio of CaO to FeO + Fe_2O_3 the change in this ratio due to oxygen evolution being so small as to be negligible. The results obtained are shown in Fig 42, curve I showing equilibrium conditions in melts of the original composition $CaO.Fe_2O_3$ and curve II in melts in which the Fe_2O_3 was originally in excess of the CaO in the molecular ratio 1.64:1. The curves on which this latter curve is based are shown in Fig. 40. It should be pointed out that the melt of curve VI, Fig. 40 had been previously melted and even though it was allowed to freeze under the highest possible

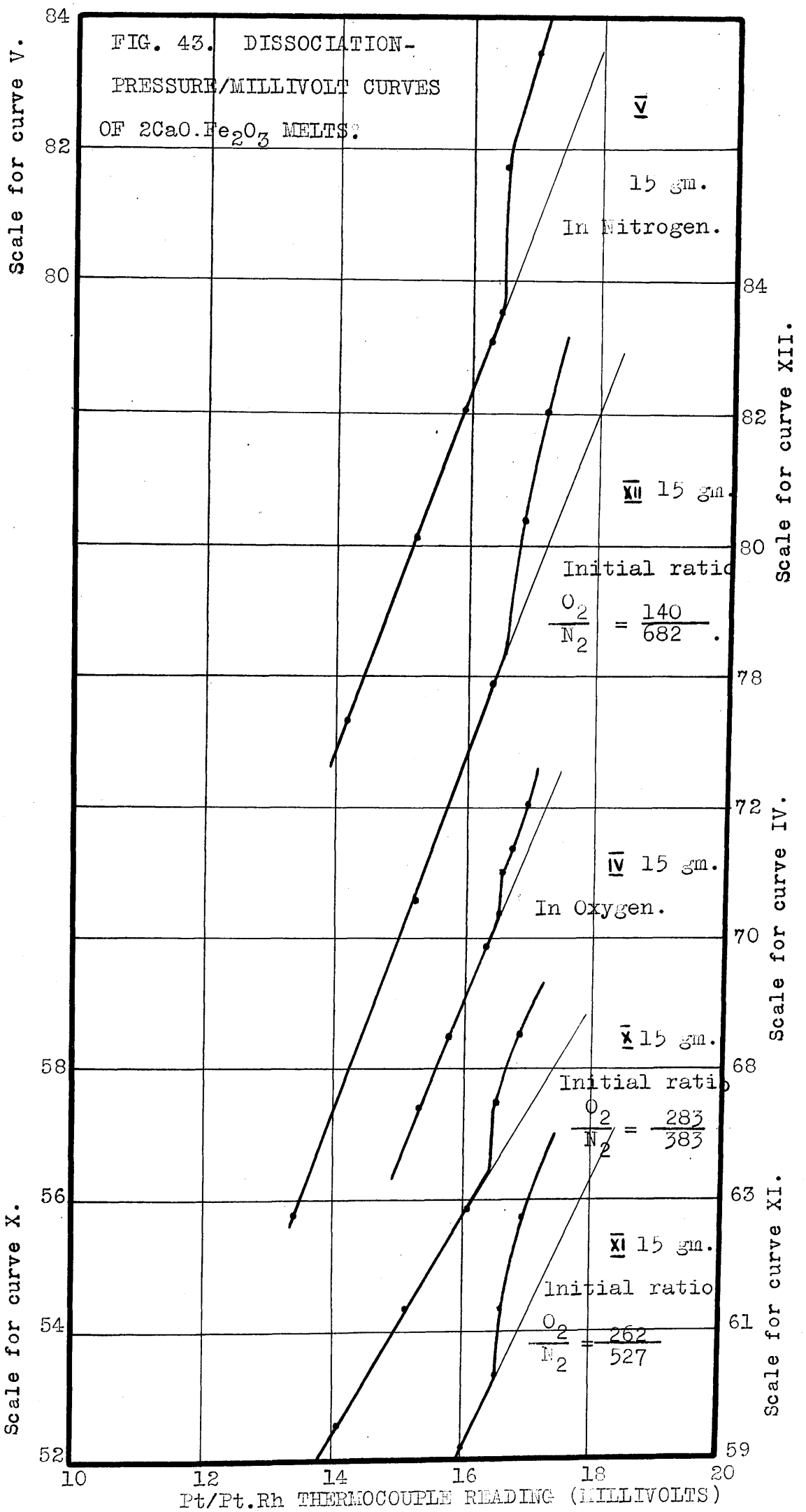
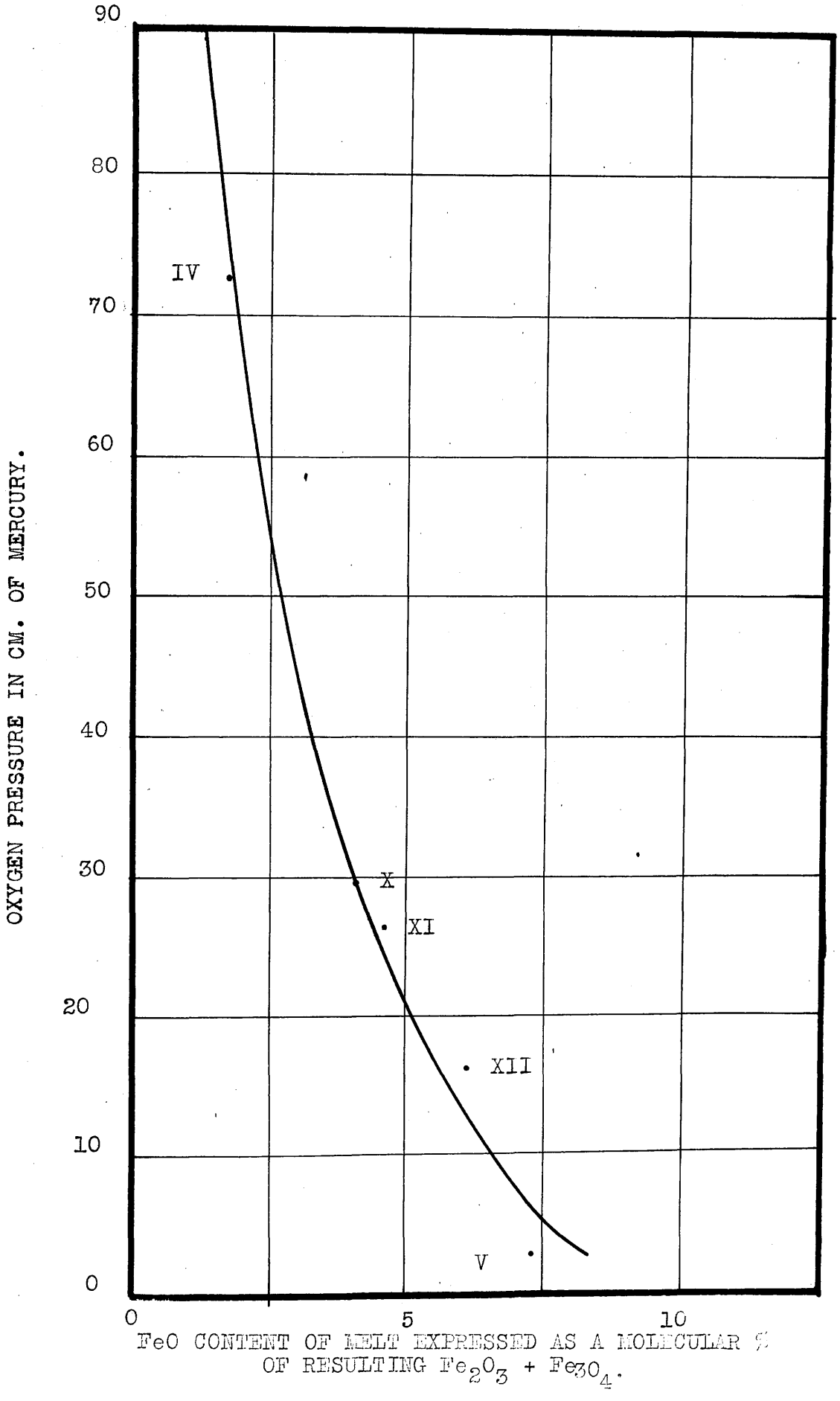


FIG. 43. DISSOCIATION-PRESSURE/MILLIVOLT CURVES OF 2CaO.Fe2O3 MELTS.
V 15 gm. In Nitrogen.
XII 15 gm. Initial ratio O2/N2 = 140/682.
IV 15 gm. In Oxygen.
X 15 gm. Initial ratio O2/N2 = 283/383
XI 15 gm. Initial ratio O2/N2 = 262/527
Scale for curve V.
Scale for curve XII.
Scale for curve IV.
Scale for curve X.
Scale for curve XI.
PRESSURE IN CM. OF MERCURY.
Pt/Pt.Rh THERMOCOUPLE READING (MILLIVOLTS)
84
82
80
78
72
70
68
63
61
59
58
56
54
52
10
12
14
16
18
20

FIG. 44. PRESSURE/COMPOSITION CURVES OF MELT OF ORIGINAL COMPOSITION $2CaO.Fe_2O_3$. AT 1485°C.



oxygen pressure it is improbable that all the iron oxide would be converted back to the ferric state. The upper point on curve II, Fig. 42 will therefore be displaced somewhat to the left of its true value.

Dicalcium Ferrite: The investigation of the dissociation of dicalcium ferrite was rendered difficult by the inability of the tubes to stand up to the higher temperatures involved when the pressure inside was much below atmospheric. It was possible however, to heat the compound in vacuo to temperatures in excess of the peritectic temperature of the monocalcium compound and no rise in pressure was apparent. Hence it is evident that the oxygen pressure of this compound is too small for measurement below the melting point. A run was also made with oxygen in the tube at a pressure of over 1 atmosphere. At 1436°C, the temperature of the peritectic transformation of dicalcium ferrite, a distinct step was obtained as shown in curve IV, Fig. 43. When an approximately similar pressure of nitrogen was employed as in curve V Fig. 43 a much larger step was obtained at the same temperature. The same considerations, therefore, seem to apply to this compound as to the monocalcium compound, the rise in pressure being probably due to the dissociation of Fe_2O_3 liberated at the peritectic.

A series of runs was carried out with varying mixtures of oxygen and nitrogen at a pressure of approximately one atmosphere in the tube. The curves obtained are reproduced in Fig. 43 with details of the weights taken and of the proportions of oxygen and nitrogen employed. With the apparatus available it was impossible to displace the initial oxygen evolution to higher temperatures. The reason is obvious from a consideration of the dissociation pressure curve of pure Fe_2O_3. A pressure of the order of thousands of atmospheres would be necessary. By the methods already described the molecular percentage of FeO reckoned against the total $FeO + Fe_2O_3$ was again calculated for different pressures of oxygen in the tube, this time at a temperature of 1485°C.

The results, plotted against oxygen pressure, are shown in Fig. 44, the curve being apparently of the same form as that obtained in the case of monocalcium ferrite at 1272°C.

SIGNIFICANCE OF THE EXPERIMENTAL RESULTS:

Fe_2O_3 on heating to high temperatures tends to dissociate, the dissociation pressure increasing rapidly at temperatures over 1200°C. The FeO or Fe_3O_4 formed by this dissociation is, however, apparently soluble to a limited extent in the remaining Fe_2O_3, the result being the formation of a solid solution with a dissociation pressure considerably lower than that of the pure ferric oxide. Nevertheless, the dissociation pressure of this solid solution,,even when saturated with Fe_3O_4, also increases rapidly at temperatures over 1400°C. For instance, at 1450°C it has reached a value of over an atmosphere. Hence, unless the oxygen pressure in the surrounding atmosphere reaches this value complete dissociation of the Fe_2O_3-rich solid solution will take place with the formation of Fe_3O_4 containing Fe_2O_3 in solution,,the exact composition depending on the oxygen pressure. To cause dissociation to proceed past the stage of Fe_3O_4 very high vacua or very high temperatures (or both) owing to its low dissociation pressure and great stability. In other words, by virtue of the formation of the stable complex Fe_3O_4, FeO can stabilize an equivalent amount of Fe_2O_3.

The action of CaO is essentially similar in nature, being the result of the formation of stable compounds, namely the calcium ferrites. These are apparently completely stable in the solid state. On melting, due to the peritectic dissociation which they undergo, they develope an oxygen pressure. The value of this dissociation pressure from the pure melts is probably the same as the pressure from Fe_2O_3 uncontaminated with any ferrous iron. (Compare Figs. 33 and 41). Immediately dissociation takes place, however, the conditions in the two cases are different, and the ratio of ferrous oxide to ferric oxide for a given temperature and oxygen pressure differs very

considerably in the two cases. The amount of dissociation taking place in monocalcium ferrite melts at 1272°C at oxygen pressures over 5 cm. of mercury is actually greater than that taking place in pure Fe_2O_3 under the same conditions. This can be seen by comparing the Fe_2O_3-Fe_3O_4 isotherm at 1272°C (Fig. 36) with the pressure/composition curve of $CaO.Fe_2O_3$ (Fig. 42) allowing for the fact that the former is expressed in molecular percentages of Fe_3O_4 and the latter in molecular percentages of FeO. Thus there seems to be a greater tendency for ferrous iron to form initially in the ferrite than in the Fe_2O_3. This may be due to the different conditions existing in the liquid and solid states, as the ferrite is molten at this temperature. Once this degree of dissociation has taken place, however, the resultant melt is much more stable than the mixture of oxides obtained from the pure Fe_2O_3. For example on decreasing the oxygen pressure to very low values, to 1 cm. of mercury say, it is shown by the Fe_2O_3-Fe_3O_4 isotherm that dissociation will proceed till the Fe_3O_4-rich solid solution is formed. The ferrite melt will only dissociate till approximately 7% of FeO is formed (reckoned as a percentage of the total iron oxides). Again, comparing the effects of rising temperature, the shape of the individual pressure/temperature curves of Fe_2O_3 given in Fig. 32a and b should be contrasted with the shape of those for $CaO.Fe_2O_3$ given in Figs. 38 and 39. Allowing for differences in weights taken the increase of the oxygen evolution from the initially pure Fe_2O_3 is much larger than that from the ferrite. It is thus evident that lime has a marked stabilizing effect on Fe_2O_3 at high temperatures after a certain initial degree of dissociation has taken place. In other words, the initial dissociation pressure is probably the same in both cases, but in the case of the ferrite melt the presence of a very small amount of FeO is sufficient to cause the dissociation pressure to drop to very low values. Though a similar drop takes place with initially pure Fe_2O_3 in the presence of FeO this is very much less pronounced and dissociation at high temperatures (and under

ordinary oxygen pressures) tends to proceed until the complete conversion of all the oxide to Fe_3O_4 has taken place.

A complete pressure/composition curve for monocalcium ferrite is only available for 1272°C at present. The only guide as to the extent of dissociation at higher temperatures is provided by the trend of the individual pressure/temperature curves which in most cases are not continued much above 1300°C. This may probably be expected to increase considerably at temperatures round about 1600°C(see for instance the upward trend of certain of the curves of Fig. 38). Fig. 44, however, shows the conditions existing in a melt of the dicalcium compound at 1485°C. With initially pure Fe_2O_3 at this temperature the dissociation, even at oxygen pressures of half an atmosphere, would be of the order of 90%, i.e. practically complete conversion to Fe_3O_4 would result. Fig. 44 shows only 4% of FeO at an oxygen pressure of 30cm. of mercury, and approximately 6% at 10cm. of mercury. This indicates the great stability of the Fe_2O_3 in melts in which the molecular ratio of CaO to oxides of iron is as 2:1. This stability appears to depend on the lime content of the melt, the dicalcium compound, for instance, being much more stable than the monocalcium compound.

Hence it is to be expected that in a slag containing excess of CaO in presence of FeO under given conditions of temperature and oxygen pressure oxidation will take place until the oxygen pressure of the slag is equal to that of the atmosphere. For a given lime content there will be, as indicated by the above results, a given equilibrium ratio of Fe_2O_3 to FeO (which will vary with temperature and oxygen pressure). Once this ratio has been attained oxidation will cease. The active lime content in this respect will presumably be the free lime after combination with SiO_2 and P_2O_5 has taken place. In a basic slag in contact with the metal bath there will be a constant tendency for this ratio to be attained, while simultaneously the reduction of Fe_2O_3 by the molten iron is taking place. In this way the slag will "convey" oxygen to the bath. The theory of the function

of lime in the basic open hearth process as advanced by McCance (l.c.) and others seems, therefore, to be in the main correct.

One of the essential differences between the acid and basic processes would seem to be that the equilibrium ratio of Fe_2O_3 to FeO in the slag is probably much greater under given conditions in the latter case than in the former.

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APPENDIX.

METHOD OF CALCULATING THE COMPOSITION OF THE SOLID PHASE FOR THE ISOTHERMS OF FIG. 36.

From the individual pressure-temperature curves, examples of which are shown in Fig. 32 (a) and (b), the composition of the solid phase was obtained in the following manner.

At a temperature of 1272°C (14.00 m.v. on the thermocouple) curve XVII, Fig. 32(a) shows a pressure in the tube of 4.00 cm. of mercury. By producing the linear portion of the curve it is seen that, if there had been no evolution of oxygen from the Fe_2O_3, the pressure would have been 2.90 cm. of mercury at this temperature. There is therefore an increase due to oxygen liberation of 1.10 cm. of mercury.

As determined empirically, the pressure in the tube increases 2.23 times between room temperature and 1272°C (the"expansion factor" mentioned in the text). Hence the equivalent difference of pressure at room temperature (22°C) = 0.493 cm. of mercury.

Volume of apparatus = 1800 c.c.

Hence, weight of oxygen liberated = 0.0145 gm.

Original weight of Fe_2O_3 = 3.0020 gm.

Hence molecular percentage of Fe_3O_4 = 10.88% at an oxygen pressure of 4.00 cm. of mercury.

By this method a series of compositions corresponding to various pressures were calculated for the temperatures 1200°C, 1272°C, 1345°C and 1415°C (corresponding to 13.00, 14.00, 15.00 and 16.00 m.v. respectively).

The actual weights of Fe_2O_3 taken were varied. For example, in Fig. 32(a) curves XVI, XVII,XVIII were obtained using 3.0020 gm. Fe_2O_3 and curves XIII, XIV,XV with 9.7243 gm. Curves XIV and XV were got after curve XIIIhad been completed, by drawing off known amounts of oxygen, so that, even with all the oxygen in the tube combined with the oxide, there would still have been some Fe_3O_4 present. In the calculations based on these curves this had to be taken into account.

The table of values obtained for the isotherm at 1345°C is

ISOTHERM AT 1345°C.

(15.00 m.v.)

"Expansion factor"= 2.30.

Ref^{ce} no. of curve.	Equilib^{m} pressure (cm. of mercury)	Pressure due to initial O_2 in tube (cm)	Diff^{ce}. (cm.)	Equiv-alent diff. at room temp.	Vol. of appar-atus. (c.c.)	Wt. of O_2 liber-ated. (gm.)	Orig^{l} Wt. of Fe_2O_3. (gm.)	Molecular % Fe_3O_4.
IX	19.20	16.05	3.15	1.37	1800	.0428	9.7243	9.22
X	15.30	11.90	3.40	1.48	1800	.0462	9.7243	10.00
XI	24.60	22.60	2.00	0.87	1800	.0272	9.7243	5.75
XII	35.90	34.30	1.60	0.69	1800	.0218	9.7243	4.59
XIII	11.70	1.61	10.09	4.38	1800	.1370	9.7243	32.9
XIV+	11.75				1800	.1683	9.7243	42.0
XV+	11.70				1800	.2668	9.7243	75.5
XVI	11.80	8.85	2.95	1.28	1800	.0401	3.0020	30.9
XVII	9.10	3.05	6.05	2.63	1800	.0824	3.0020	75.4
XVIII	7.50	1.80	5.70	2.48	1800	.0775	3.0020	69.5
XXII	39.40	37.90	1.50	0.65	1850	.0210	12.9020	3.31
XXIII	67.40	66.60	.80	0.35	1850	.0112	12.9020	1.77
XXVI	41.90	39.60	2.30	1.00	1850	.0322	21.1195	3.11
XXVII	55.70	54.20	1.50	0.65	1850	.0210	21.1195	2.01
XXVIII	75.30	74.00	1.30	0.56	1850	.0182	21.1195	1.74

+ The calculations from curves XIV and XV were obtained indirectly as explained above.

given below as an example.